ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

CORROSION AND OTHER ASPECTS RELATIVE TO THE USE OF
DIPHENYL AS A COOLANT-MODERATOR

by

Gustave C. Milak

Reactor Engineering Division

November, 1956

Operated by The University of Chicago
under
Contract W-31-109-eng-38

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	5
I. STATIC CORROSION TESTS.	5
A. Introduction.	5
B. Experimental.	6
1. Equipment.	6
2. Materials and Material Preparation.	8
3. Procedure.	8
C. Results.	9
D. Discussion	23
E. Conclusions.	24
II. CONCURRENT STUDIES WITH DIPHENYL.	25
A. Falex Test Evaluation of Lubricity of Diphenyl vs Water	25
1. Group I - Moderate Applied Loading	25
2. Group II - Low Applied Loading	28
B. Burnout Tests for Diphenyl and Water	29
C. Shutdown Poisons	30
D. Evaluation of Methods of Coating Uranium for Use in Diphenyl	31
1. Enamel Coating	31
2. Metal Coating	32
APPENDIX A	35

LIST OF TABLES

<u>Number</u>	<u>Title</u>	<u>Page</u>
I	Summary of Static Corrosion Tests in 500F Diphenyl	10
II	Summary of Corrosion Tests in 680F and 750F Diphenyl	10
III	Summary of Supplementary Static Corrosion Tests in 750F and 680F Diphenyl	11
IV	Summary of Static Corrosion Tests on Control Rod Materials in 500F Diphenyl	11
V	Summary of Static Corrosion Tests in 500F Diphenyl with 500 psi Nitrogen	11
VI	Summary of Static Corrosion Tests on Zirconium and Zirconium Alloys in 750F and 680F Diphenyl.	12
VII	Static Corrosion Tests in 500F Diphenyl.	36
VIII	Static Corrosion Tests in 680F and 750F Diphenyl	38
IX	Supplementary Static Corrosion Tests in 750F and 680F Diphenyl	40
X	Static Corrosion Tests on Control Rod Materials in 500F Diphenyl	41
XI	Static Corrosion Tests in 500F Diphenyl with 500 psi Nitrogen	42
XII	Static Corrosion Tests on Zirconium and Zirconium Alloys in 750F and 680F Diphenyl	43

4

ACKNOWLEDGEMENT

The author gratefully acknowledges the assistance rendered by Messrs. L. W. Fromm, G. A. Freund, C. R. Breden, and L. A. Hasenfang during the course of the investigation.

CORROSION AND OTHER ASPECTS RELATIVE TO THE USE OF DIPHENYL AS A COOLANT-MODERATOR

by
Gustave C. Milak

ABSTRACT

In over 4500 hr of testing in static diphenyl at 500F, 680F, and 750F, uranium and high-uranium alloys showed considerably lower corrosion rates and no tendency toward catastrophic failure by comparison with their counterparts in high-temperature water. Corrosion of structural and cladding materials was, in general, equivalent to that of stainless steel in water. Diphenyl showed much better lubricating qualities than water. Burnout heat fluxes of 500,000 Btu/(hr)(sq ft) were attained in stagnant, subcooled diphenyl at atmospheric pressure. Based on physical properties and solubility tests, boric acid esters showed promise as shutdown poisons for diphenyl reactors. Samples representative of two methods of coating uranium (as contrasted to cladding) were investigated. The technology does not appear sufficiently advanced for these coatings to fulfill the stringent requirements of a sole barrier between uranium and the diphenyl coolant.

I. STATIC CORROSION TESTS

A. Introduction

The proposal for using diphenyl as a coolant-moderator offers the possibility of major reductions in cost and complexity of nuclear reactor systems, as, for example, with the use of conventional materials such as carbon steel in the reactor primary system; the use of thin fuel element cladding of inexpensive, higher cross-sectional materials than zirconium; and, under certain conditions, the use of unclad fuel elements.

Exploratory tests were conducted in 1953 with relation to the corrosion of uranium and magnesium in 500F diphenyl. The results, when compared to water corrosion, were sufficiently promising to warrant a more comprehensive study of the corrosion characteristics of various reactor materials in diphenyl at 500F and higher temperatures. Observations made during the earlier tests also demonstrated the necessity for excluding air and water vapor from the test solution.

365 005

365 005

B. Experimental Equipment and Procedure

1. Equipment

The tests were performed in 100-ml capacity, stainless steel (Type 304 or Type 347) autoclaves (Fig. 1). The sample holders were made of stainless steel and were designed to hold the specimens in an upright position to minimize contact with the holder and to permit free access of test solution. The autoclaves containing 50 ml diphenyl were heated in K. H. Huppert Electric Furnaces (Fig. 2), designed to hold 24 autoclaves.

FIG. 1
AUTOCLAVE COMPONENTS

In order to control pressure, the tests with 500 psi nitrogen on the diphenyl were conducted in a special autoclave equipped with a pressure gauge, a connection to the nitrogen supply, and a heating jacket.

FIG. 2
HUPPERT FURNACE USED BY ARGONNE
TO HEAT AUTOCLAVES FOR STATIC TESTS

2. Materials and Material Preparation

a. Biphenyl (Diphenyl; Phenyl Benzene)

Properties of Pure Material

Molecular Weight	154.20
Boiling Point at 760 mm	255C
Boiling Point at 10.5 mm	118C
Crystallizing Point	69C
Melting Point	69C
Specific Gravity at 77C	0.9896
Specific Gravity at 20C	1.041
Solubility in Water	--
Flash Point	
closed cup	235F
open cup	255F
Weight per gal at 77C	8.23 lb

Bulk diphenyl used throughout the tests was stored in fiber cartons at room temperature.

b. Specimen Preparation

Material permitting, all samples were sawed and/or machined to a standard sample size. The dimensions of the majority of samples were $1\frac{1}{2} \times 3\frac{3}{4}$ in., with thicknesses varying from 0.059 to 0.071 in. Whenever a new group of specimens were fabricated for tests at the various temperatures, the original stock was used; thus, the uranium, uranium-zirconium, etc., tested in the 500F diphenyl was of the same stock as that tested in the 680-750F diphenyl.

Samples were scrubbed, thoroughly dried and then degreased in trichlorethylene. Only four of the entire group of samples, namely, two specimens each of Zircaloy 2 and Zircaloy 3, were pickled. All sample holders and autoclaves were pickled in HF-HNO₃ solution before the test program was started. Samples were put into test as soon as possible after degreasing and weighing.

3. Procedure

Approximately fifty grams of dry diphenyl were packed into the prepared autoclave. Heat was applied (gas-oxygen flame) to the lower outside portion of the autoclave until the temperature of the diphenyl reached 150C (300F). After a heavy evolution of diphenyl vapor for approximately five seconds, the sample holders and samples were immersed slowly into the molten diphenyl (during the later tests, the diphenyl was heated to the boiling point). The gasket seal and plug were inserted and the cover was

9
applied and tightened mechanically. The autoclave was placed in the furnace having required temperature. Due to the large number of samples and limited supply of autoclaves, samples of similar materials were tested in the same autoclave.

After the required exposure time, the autoclaves were removed and allowed to stand at room temperature for approximately 45 min for the 500F tests, and one hour for the 680F and 750F tests, before opening. Samples were then immediately removed from the hot diphenyl and placed in a container of trichlorethylene. The autoclave was resealed immediately. After a minimum of 30 min in the solvent to dissolve the excess diphenyl, the samples, after a gentle swirling, were removed, oven dried at about 100F for one hour and then weighed. Throughout the entire series of tests, the samples were handled as gently as possible and then only with stainless steel tweezers. Any additional handling was done with white cotton gloves.

The same diphenyl in each autoclave was used throughout all the tests except in those cases where autoclaves were reported dry or a partial loss of diphenyl brought the liquid level below the necessary volume requirement. Such refillings or additions were noted and recorded.

C. Results

Results of the static corrosion tests are summarized in Tables I through VI in terms of a weight change rate for the entire exposure. Pictorial views of the sample appearance at the conclusion of each test are shown in Figs. 3 to 21. The latter are adjudged to be of equal importance in the over-all evaluation, since, despite all precautions in handling the specimens, the surface corrosion products may have been disturbed, even lost, and, as a consequence, have affected the reported corrosion rate.

A detailed history of the respective tests is given in Appendix A.

Table I

SUMMARY OF STATIC CORROSION TESTS IN 500F DIPHENYL

Sample No.	Material	Sur-face Area, cm ²	Total Ex-posure, hr.	Weight, gm		Wt. chg., mg/(cm ²)(mo)	Ref. Fig.
				Before	After	ΔWt	
A-4413-2	U-2% Zr	8.4	4508	10.4972	10.2828	-0.2144	5
A-4413-2A	U-2% Zr	8.4		10.2650	9.9706	-0.2944	5
A-4414-1	U	16.3		22.1762	21.7580	-0.4182	3
A-4415-3	U-5% Zr	16.2		19.6240	19.3338	-0.2902	6
A-4416-4	U-1.5% Nb-5% Zr	16.3		19.7151	19.6850	-0.0301	7
A-4417-5	U-2% Mo	16.5		22.3216	22.0641	-0.2575	4
A-4418-12	Nickel "A"	16.3		10.1532	10.1524	-0.0008	15
A-4419-11	Carbon Steel						
	SAE 1020	16.6	4508	10.4404	10.4403	-0.0001	13
A-4424-7	U-91.8% Al	16.1	4463	3.0570	3.0566	-0.0004	9
A-4425-8	Zircaloy 2	16.9		7.8053	7.8071	+0.0018	-
A-4426-9	2S Al	16.3		3.3671	3.3670	-0.0001	10
A-4427-10	Magnesium Dow Pure	8.75		0.9836	0.9835	-0.0001	16
A-4427-10A	Magnesium Dow Pure	8.75		1.0094	1.0086	-0.0008	16
A-4428-14	Al 99.1%-Ni 0.9%	16.2		3.1668	3.1668	±0.000	12
A-4429-16	Aluminum Alloy X-2219	16.3		3.3290	3.3291	+0.0001	11
A-4430-15	U 9% - Zr 88.5% - Sn 2.5%	15.9		6.5348	6.5361	+0.0013	8
A-4431-13	Type 347	16.4	4463	9.3160	9.3157	-0.0003	14

Table II

SUMMARY OF CORROSION TESTS IN 680F AND 750F DIPHENYL

Sample No.	Material	Sur-face Area, cm ²	Total Ex-posure, hr.	Weight, gm		Wt. chg., mg/(cm ²)(mo)	Ref. Fig.
				Before	After	ΔWt	
A-4433-1	U	16.3	2310	21.6194	Sample Disintegrated		
A-4434-2	U-2% Zr	8.4	6919	10.4300	10.0794	-0.3506	5
A-4434-2A	U-2% Zr	8.4	6919	10.2786	9.7982	-0.4804	5
A-4435-3	U-5% Zr	16.2	6919	19.6443	19.3531	-0.2912	6
A-4436-4	U-5% Zr-1.5% Nb	16.3	6919	19.7406	19.4985	-0.2421	7
A-4437-5	U-2% Mo	16.5	3094	21.7836	Sample Disintegrated		
A-4438-7	U-91.8% Al	16.1	4718	3.5662	3.5657	-0.0005	9
A-4439-8	Zircaloy 2	16.9	4718	7.7762	7.8015	+0.0253	
A-4440-9	2S Al	16.3	4718	3.3412	3.3404	-0.0008	10
A-4441-10	Magnesium Dow Pure	16.2	4718	2.0177	1.9419	-0.0758	16
A-4442-11	Carbon Steel						
	SAE 1020	16.6	4718	10.4643	10.4798	+0.0155	13
A-4443-12	Nickel "A"	16.9	4718	10.0455	10.0451	-0.0004	15
A-4444-13	Type 347	16.4	4718	9.3594	9.3590	-0.0004	14
A-4445-14	Al 99.1% - Ni 0.9%	16.2	4718	3.1684	3.1677	-0.0007	12
A-4446-15	U 9% - Zr 88.5% - Sn 2.5%	15.9	6919	6.6577	6.3764	-0.2813	8
A-4447-16	Aluminum Alloy X-2219	16.3	4718	3.3277	3.3276	-0.0001	11

Table III

SUMMARY OF SUPPLEMENTARY STATIC CORROSION TESTS IN 750F AND
680F DIPHENYL (3562 HR AT 750F; 263 HR AT 680F)

Sample No.	Material	Sur- face Area, cm ²	Total Ex- posure, hr.	Weight, gm		Δ Wt	Wt. chg., mg/(cm ²)(mo)	Ref. Fig.
				Before	After			
A-4545-1B	U	7.8	3825	10.0381	9.9213	+0.1168	-2.81	3
A-4547-1A	U	8.3	3825	10.8390	10.7217	+0.1173	-2.65	3
A-4546-5B	U-2% Mo	8.4	3825	10.6603	10.5530	+0.1073	-2.40	4
A-4548-5A	U-2% Mo	7.9	3825	9.7836	9.6917	+0.0919	-2.19	4
A-4550-8A	Zircaloy 2	16.9	3825	7.8012	7.8239	+0.0227	+0.252	20
A-4549-16A	Aluminum Al- loy X-2219	16.3	3825	3.3275	3.3283	+0.0008	+0.009	11

Table IV

SUMMARY OF STATIC CORROSION TESTS ON CONTROL ROD MATERIALS IN 500F DIPHENYL

Sample No.	Material	Sur- face Area, cm ²	Total Ex- posure, hr.	Weight, gm		Δ Wt.	Wt. chg., mg/(cm ²)(mo)	Ref. Fig.
				Before	After			
A-4551	1.2% Boron Steel	16.4	3635	8.9555	8.9559	+0.0004	+0.005	18
A-4552	2.02% Boron Steel	16.8	3635	11.5393	11.5393	$\pm$ 0.0	$\pm$ 0.0	18
A-4553	Cd 30% - Ag 70%	17.5	3635	19.6412	19.6380	-0.0032	-0.036	17
A-4554	2.18% Boron Steel	17.1	3635	12.9090	12.9094	+0.0004	+0.004	18
A-4555	0.97% Boron Steel	16.4	3635	9.3028	9.3034	+0.0006	+0.007	18
A-4556	Graphitars No. 14, 38, 30, 41		3635	No physical change				

Table V

SUMMARY OF STATIC CORROSION TESTS IN 500F DIPHENYL WITH 500 PSI NITROGEN

Sample No.	Material	Sur- face Area, cm ²	Total Ex- posure, hr.	Weight, gm		Δ Wt.	Wt. chg., mg/(cm ²)(mo)	Ref. Fig.
				Before	After			
A-4585	Zircaloy 2	16.9	2566	7.7083	7.7106	+0.0023	+0.038	20
A-4586	2S Al	16.3	2566	3.2358	3.2361	+0.0003	+0.005	10
A-4587	Magnesium Dow Pure	16.2	2566	2.0266	2.0316	+0.0050	+0.080	16
A-4584-2	U-2% Zr	8.4	-	-	-	Sample Disintegrated		
A-4584-2A	U-2% Zr	8.4	-	-	-	Sample Disintegrated		
A-4596	U-91.8% Al	15.2	2029	3.2587	3.2590	+0.0003	+0.006	9

Table VI

SUMMARY OF STATIC CORROSION TESTS ON ZIRCONIUM AND ZIRCONIUM
ALLOYS IN 750F AND 680F DIPHENYL

Sample No.	Material	Sur- face Area, cm ²	Total Ex- posure, hr.	Weight, gm		Wt. chg., mg/(cm ²)(mo)	Ref. Fig.
				Before	After		
A-4597-A	Zr-Sponge	9.36	2051	7.5968	7.5990	+0.0022	19
A-4597-B	Zr-Sponge	8.69	2051	5.3167	5.3179	+0.0012	19
A-4598-A	Zr-Grade III	7.1	2051	8.8441	8.8496	+0.0055	19
A-4598-B	Zr-Grade III	7.1	2051	8.8346	8.8409	+0.0063	19
A-4599-A	Zr-Grade I	7.1	2051	9.0648	9.0713	+0.0065	19
A-4599-B	Zr-Grade I	7.1	2051	9.0675	9.0746	+0.0071	19
A-4600-A	Zircaloy 2	17.8	2051	15.1109	15.1176	+0.0057	20
A-4600-B	Zircaloy 2	17.8	2051	14.9293	14.9361	+0.0068	20
A-4601-A	Zircaloy 3	16.4	2051	7.6942	7.7027	+0.0085	21
A-4601-B	Zircaloy 3	16.4	2051	7.8403	7.8472	+0.0069	21
A-4602-C	Zircaloy 3 (pickled)	16.4	2005	7.6616	7.6645	+0.0029	21
A-4602-D	Zircaloy 3 (pickled)	16.4	2005	7.7754	7.7776	+0.0022	21
A-4603-C	Zircaloy 2 (pickled)	18.1	2005	14.8427	14.8472	+0.0045	20
A-4603-D	Zircaloy 2 (pickled)	18.1	2005	14.9938	14.9973	+0.0035	20

13
A-4414-1 A-4545-1B A-4547-1A
500 F 750 F & 680 F

4508 HRS

3825 HRS

3825 HRS

FIG. 3
URANIUM

A-4417-5 A-4546-5B A-4548-5A
500 F 750 F & 680 F

4508 HRS

3825 HRS

3825 HRS

FIG. 4
URANIUM - 2% MOLYBDENUM

A-4413-2 A-4413-2A A-4434-2 A-4434-2A
500 F 680 F & 750 F

4508 HRS 4508 HRS 6919 HRS 6919 HRS

FIG. 5
URANIUM - 2% ZIRCONIUM

A-4415-3 A-4435-3
500 F 680 F & 750 F

4508 HRS 6919 HRS

FIG. 6
URANIUM - 5% ZIRCONIUM

A-4416-4 A-4436-4
500 F 680 F & 750 F

4508 HRS 6919 HRS

FIG. 7
URANIUM - 5% ZIRCONIUM - 1.5% NIOBIUM

A-4430-15

500 F

A-4446-15

680 F & 750 F

4463 HRS

6919 HRS

FIG. 8
URANIUM - 88.5% ZIRCONIUM - 2.5% TIN

A-4424-7

500 F

A-4438-7

680 F & 750 F

A-4596

500 F-500 PSI-N₂

4463 HRS

4718 HRS

2029 HRS

FIG. 9
URANIUM - 91.8% ALUMINUM

FIG. 10
ALUMINUM 2S

FIG. 11
ALUMINUM ALLOY X2219

A-4428-14

A-4445-14

500 F

680 F & 750 F

4463 HRS

4718 HRS

FIG. 12
ALUMINUM 99.1% - NICKEL 0.9%

A-4419-11

A-4442-11

500 F

680 F & 750 F

4508 HRS

4718 HRS

FIG. 13
CARBON STEEL SAE 1020

A-4431-13

A-4444-13

500 F

680 F & 750 F

4463 HRS

4718 HRS

FIG. 14
STAINLESS STEEL TYPE 347

A-4418-12 A-4443-12
500 F 680 F & 750 F

4508 HRS 4718 HRS

FIG. 15
NICKEL A

A-4427-10 A-4427-10A A-4441-10 A-4587
500 F 500 F 680 F & 750 F 500 F-500 PSI-N₂

4463 HRS 4463 HRS 4718 HRS 2566 HRS

FIG. 16
MAGNESIUM DOW PURE

A-4553-100

500 F

3635 HRS

FIG. 17
CADMIUM 30% - SILVER 70%

A-4551-200

500 F

3635 HRS

A-4552-300

500 F

3635 HRS

A-4554-400

500 F

3635 HRS

A-4555-500

500 F

3635 HRS

1.2% BORON

2.02% BORON

2.18% BORON

0.9% BORON

FIG. 18
BORON STEEL

A-4597-A

A-4597-B

750 F & 680 F

2051 hrs

2051 hrs

SPONGE

A-4599-A

A-4599-B

A-4598-A

A-4598-B

750 F & 680 F

750 F & 680 F

2051 hrs

2051 hrs

2051 hrs

2051 hrs

GRADE I

GRADE III

FIG. 19
ZIRCONIUM

FIG. 20
ZIRCALOY 2

FIG. 21
ZIRCALOY 3

D. Discussion

In 500F diphenyl, uranium and high-uranium alloys showed no indication of the catastrophic failure characteristic of exposure in high-temperature water. The long-term weight loss rates of about 5 mg/(cm²) (mo) are considerably lower than those of the best comparable materials in water at that temperature.

The general trends hold true for the 680 and 750F exposure, although the results are somewhat inconsistent. Some samples show higher rates than at 500F and others show lower rates. This inconsistency may be attributed to the unknown fabrication history of the samples which were cut from available stock.

There were two cases of failure in the 680F tests (Table II). The uranium sample (No. A-4433-1) showed signs of surface cracking after 1163 hr and after an additional 1147 hr was found to be disintegrating. The uranium-2% molybdenum sample tested in the same autoclave (No. A-4437-5) showed signs of surface blistering and laminar cracking after 2310 hr; after an additional 784 hr disintegration was noted.

X-ray diffraction analysis of the disintegrated samples by the Argonne Metallurgy Division revealed the formation of the carbide of uranium. The corrosion products on both samples were also analyzed chemically, with the following results:

Carbon:	4.46 to 4.56%
Nitrogen:	125 to 136 ppm
Hydrogen:	0.05 to 0.08%

In order to determine whether an accidental firing of diphenyl (during sample loading) with subsequent carbon deposit in the autoclave may have contributed to the failure of the sample, one autoclave containing these materials was ignited deliberately and sealed after the flame was extinguished. A second autoclave containing identical samples was loaded in accordance with the standard procedure.

However, the conditions were apparently not duplicated since the accumulated test time exceeded the period at which the earlier disintegration had occurred. After 3825 hr (Table III) both flashed and unflashed test specimens exhibited very little weight change variation. Visible differences in appearance were negligible.

The known affinity of uranium for nitrogen was demonstrated when the two samples of uranium-2% zirconium (Table V) showed signs of disintegration after only 337 hr in 500F diphenyl pressurized with 500 psi nitrogen. Analysis of the corrosion products and results of diffraction patterns showed the formation of UN₂.

The uranium-91.8% aluminum alloy, such as might be used in a fully enriched reactor, showed excellent corrosion resistance at all three temperatures. The uranium-88.5% zirconium-2.5% tin alloy showed a rather high rate at the higher temperatures.

At 500F all the structural and cladding materials showed low corrosion rates. With the exception of magnesium, the rates at 680F and 750F were considered satisfactory. The weight gain rates on zirconium and Zircaloy at these temperatures were somewhat higher than might have been expected, but surface appearances were satisfactory. X-ray diffraction at KAPL¹ showed the coating to be zirconium oxide, indicating the importance of impurity control in the diphenyl. Nitrogen pressure at 500F had no effect on the structural materials.

The corrosion resistance of control rod materials after 3635 hr in 500F diphenyl is comparable to that of the best structural materials. The cadmium-silver alloy, which must be used clad in high-temperature water, showed an over-all weight change of $-0.036 \text{ mg}/(\text{cm}^2)(\text{mo})$. The four Graphitar samples included in these tests showed no visible change in appearance or geometry after the same number of test hours.

E. Conclusions

The reduced corrosion attack by static diphenyl at 500F, 680F, and 750F on fuel, control rod and structural materials, as compared to water, has been established.

In over 4000 hr at the three temperatures, uranium and high-uranium alloys have shown no real tendency toward catastrophic failure.

Structural, as well as control rod, materials exhibited extremely encouraging corrosion resistance and generally no more attack than stainless steel in water at the same temperatures.

Careful control of impurities in the diphenyl is required to minimize corrosion and produce significant results.

The somewhat high weight gain rates of zirconium and Zircaloy, compared to other materials such as aluminum, while not necessarily presenting a corrosion problem, do warrant further investigation.

The inconsistency in the corrosion behavior of some of the materials may be attributed, in part, to the unknown fabrication histories of the specimens.

¹Private Communication, F. D. Leipziger

II. CONCURRENT STUDIES WITH DIPHENYL

A. Falex Test Evaluation of Lubricity of Diphenyl vs Water

1. Group I - Moderate Applied Loading

The original standard prescribed Falex tests were designed for studies and investigations up to failure of the test specimen or the test machine (Fig. 22) and were intended, primarily, to evaluate lubricants. This investigation, however, was limited to the lower applied loads. In the hope that the test sample surface condition would not seriously be marred by excessive wear, the length of run test time was held to 5 min. These tests therefore represent an initial limited evaluation of the lubricating qualities of diphenyl compared to those of water.

Since diphenyl is solid at room temperature, all tests, including those in water, were run at a lubricant temperature of 180F. Heating coils, controlled by a variable transformer at the bottom of the lubricant tray, provided the heat.

Six sets of stainless steel Type 347 and carbon steel 1020 specimens were tested. Since slight machining imperfections in the test blocks could result in irregular surface wear, the samples for each test were selected at random.

In the interests of uniformity in test methods, blocks with angles of 90 degrees were used upon recommendation of the manufacturers of the Falex test machine.

A set of conditioned test pieces or bearing blocks was placed in the test machine into self-aligning recesses in the short lever arms or jaws of the load-applying mechanism (Fig. 23). When the pre-determined temperature (180F) was reached, a minimum jaw loading of 50 lb was applied shortly after the motor (pin drive) was started. The motor pin drive was then operated for a 5-minute period at a speed of 290 rpm. A torque reading was taken a few seconds before the end of the test period. The sample pin and bearing blocks were removed and cleaned for visual and measurement check.

After the machine had cooled sufficiently, a new test assembly (blocks and pin) was inserted in the holding devices. A 1-minute run-in period at an applied load of 50 lb was started. The load was increased to 100 lb, after which the 5-minute test period commenced. This procedure was repeated at load increments of 50 lb using a new test assembly and a 50-lb, 1-minute run-in period to start each increment run. Fresh diphenyl and water were used for each test.

26

(a)
OPERATING POSITION

(b)
OPEN POSITION

FIG. 22
FALEX MACHINE

FIG. 23
WEAR TEST DEVICE

Performance curves for each of the steels in both lubricants are plotted on a basis of applied load vs torque in Fig. 24.

FIG. 24
TORQUE AS A FUNCTION OF
APPLIED LOAD FOR CARBON
STEEL AND STAINLESS STEEL
IN DIPHENYL AND IN WATER

2. Group II - Low Applied Loading

This series of tests was made with fresh samples consisting of 24 sets of cold-rolled steel blocks, 12 sets of cold-rolled steel pins and 12 sets of Type 304 stainless steel pins. The test method was modified slightly by decreasing the applied loading and increasing the test run period. This, it was felt, would more closely simulate the actual operating conditions of control rod drives and would aid in the selection of a suitable control rod mechanism for a diphenyl reactor.

The applied loading during the 1-minute run-in period was 20 lb. The tests were operated for 30 min. The applied loading ranged from 20 to 50 lb, in 5-lb increments.

Visual examination (40X magnification) of each set of test specimens in both the moderate and low applied load tests was made after each test period. The following observations were made:

(1) Diphenyl-lubricated specimens showed a more uniformly measurable scar area as evidenced by the scar (or wear) area on the test sample surface (see Fig. 25).

FIG. 25

APPEARANCE OF COLD-ROLLED STEEL FALEX TEST BEARING BLOCKS

(2) Stainless Steel Types 347, 304, carbon, and cold-rolled steels show less tendency to gall when lubricated with diphenyl.

On the basis of these tests and the chemical and physical properties of both the diphenyl and water (film strength, viscosity, corrosion characteristics), diphenyl possesses the better lubricating properties. Literature² also reveals that in many instances diphenyl additives have been used to strengthen lubricant film.

B. Burnout Tests for Diphenyl and Water

An important limitation on the heat transfer capabilities of any coolant is its burnout heat flux.

The test facility (see illustration) consisted of a copper tube ($1\frac{1}{2}$ in. ID, 2 in. long) brazed to a copper base plate which served as one

electrode. The pin holder consisted of a solid copper rod ($1/4$ in. OD, 4 in. long) drilled out at one end to accommodate $1/8$ in. OD, Type 347 stainless steel tubing. The opposite end of the tubing was similarly housed in a solid copper collar or base. Both holes were chamfered slightly. After inserting the stainless steel pin into both drilled holes the unit was brazed. Approximately $3/8$ to $7/16$ in. of effective tubing length was exposed for test. The pin holder was then inserted into the base plate, collar down, and soft soldered. The remainder of the test apparatus was designed for quick assembly and disassembly.

The copper can was filled with either molten diphenyl or water. A standard thermometer was used to measure liquid temperature. New diphenyl or water was used for each test. The can containing the diphenyl or water was placed in a galvanized, cylindrical trough through which water flowed for cooling purposes.

A high-amperage transformer provided the power. A "clamp on" ammeter and two voltmeters were used to measure the amperage and the voltage. A variac was used to control the input voltage to the transformer.

²E. N. Klemgard, "Lubricating Greases: Their Manufacture and Use" (Reinhold Publishing Company, New York, 1937).

The results, as might be expected, were considerably higher than those correlated by Rohsenow and Griffith³ for pool-boiling of saturated liquids. As shown in the tabulation, however, there is no measurable variation in burnout flux with bulk diphenyl temperature, i.e., degree of sub-cooling.

Pin No.	Medium	Heat Input		Area, sq ft x 10 ⁻³	Heat flux, Btu/(hr) (sq ft)	Coolant Temp., F
		Watts	Btu/hr			
1	Diphenyl	171.6	585	1.17	500,000	290
2	Diphenyl	149.6	510	1.01	510,000	266
3	Diphenyl	150.48	513	1.01	510,000	182
4	Water	283.2	965.7	1.01	960,000	171
5	Water	280.8	957.	1.01	950,000	*

* Not Measured

C. Shutdown Poisons

Boric acid esters would appear to have promise as emergency shutdown poisons for an organic-cooled reactor.

Of several boric acid esters available in sample quantities from Pacific Coast Borax Company, Tri-O-Cresyl Borate and Tri(2-cyclohexyl-cyclohexyl) Borate, were selected, the former because of its aromatic ring structure which should make it more stable than other esters, and the latter because of its presumably high boiling point, which would leave it behind with diphenyl decomposition products if distillation is used as the method of purification in a reactor system.

Pertinent properties are listed below:

	Tri-O-Cresyl Borate	Tri-(2-cyclohexyl-cyclohexyl) Borate
Formula	C ₂₁ H ₂₁ O ₃ B	C ₃₆ H ₆₃ O ₃ B
Mol. Weight	332.2	554.7
% Boron*	3.28%	2.03%
Density	1.079/71.6F	(?)
Boiling Point	380F (2mm)	(?)
Melting Point	-	345F

* For purposes of comparison, the percent boron in boric acid is 17.5%.

³ W. M. Rohsenow and P. Griffith, "Correlation of Maximum Heat Flux Data for Boiling of Saturated Liquids," Massachusetts Institute of Technology Technical Report No. 6 (March 1, 1955).

31

Both esters were found to dissolve very readily and rapidly in diphenyl at 200F, presumably in all proportions. (The tests were carried out to a one to one mixture.) Solutions of diphenyl and ester were crystal clear.

D. Evaluation of Methods of Coating Uranium for Use in Diphenyl

Inasmuch as uranium and high-uranium alloys showed relatively high corrosion resistance and no tendency toward catastrophic failure when exposed to high-temperature diphenyl, it appeared advisable to investigate the covering of uranium by coating rather than by cladding methods. Such methods could be less expensive and/or involve thinner coatings with higher neutron absorption cross section.

Considerable effort has been directed primarily toward the development of methods of application of diffusion and thermal barriers on uranium which is subsequently to be clad with aluminum. The purpose of the work described here is to evaluate the coating produced by these methods in terms of the more stringent requirements of being the sole barrier between the fuel and coolant.

1. Enamel Coating

Battelle has reported⁴ considerable success with enameling uranium for diffusion barrier purposes. These coatings were not intended for applications requiring resistance to corrosive conditions.

Preliminary tests were made on two typical samples prepared by methods described in the referenced document. The results indicate that enameled uranium probably would not be satisfactory for exposure to diphenyl. Microscopic examination of the coating showed some non-uniformity in the distribution of frits. In some areas this non-uniformity, characterized by a dark-reddish brown spot, was very brittle to the touch of a steel probe. As the material was carefully chipped away, a pocket or void could be observed, indicating a separation of some kind.

Scattered over the surface were small specks of what appeared to be uranium or its oxide. As these specks were scraped away carefully, breaks in the glassy coating, resembling craters, became evident. Some blistering was also observed; when broken, a cavity was revealed.

In certain areas and on the face of the enamel, a considerable amount of what appeared to be faint scratches was observed. Careful examination showed that in many cases these scratches were definite

⁴Harlan P. Tripp, et al, "Enamels and Enameling Techniques for Coating Uranium Slugs," Battelle Memorial Institute Report No. BMI-1024 (August 2, 1955).

hairline cracks. As these areas were probed, chips were removed that followed a definite geometric pattern; each chip was bordered or limited by a certain series of scratches. In one or two instances removal of the chip exposed the uranium.

A solution of potassium iodide dripping slowly on a small rectangular piece of absorbent-type neutral paper placed in the center of the slug showed the formation of iodide of uranium, indicative of a definite opening through the coating to the uranium.

Cross-sectional views of cut portions of the slug showed a comparatively uniform thickness of enamel. The slight pockets or voids previously described became evident and, in some cases, extended to the uranium. Under slight probing the coating immediately surrounding some of these areas was easily chipped off. The remainder of the coating was very difficult to dislodge, indicating a very good bond.

The test samples were coated on one side only; therefore corrosion tests were not feasible.

Thermal, shock and vibration tests would indicate the influence of stresses on the stability of the protective coating. A thermal shock test was conducted at Battelle Memorial Institute; under a quick temperature change the vitreous material disintegrated. This was particularly true of the 10 to 12-mil coatings. Thinner coatings of approximately 1 to 2 mils respond much more readily to this temperature change, although there is still some evidence of failure. It becomes evident that further experimental work in application technique, method of control and bonding of uranium with enamel is still necessary to make it suitable for this application.

2. Metal Coating

The merits of a metallic coating were considered, because such a coating would have the desirable properties of high corrosion resistance, low capture cross section for thermal neutrons, high ductility and high thermal conductivity.

A number of procedures for applying metallic coatings to uranium were investigated by Chiotti at Iowa State College.⁵ Hot-dip procedures and techniques for the various metallic coatings were described.

Two such discs were examined visually. Metal coating thickness was fairly uniform over a major portion of each disc. Coating thickness, excluding irregularities, varied from 1 to 3 mils (measured at

⁵P. Chiotti, et al., "Application of Metal Coatings on Uranium" Ames Laboratory, Iowa State College Report No. ISC-640 (September 20, 1955).

ISC). In some areas a buildup of eutectic from 5 to 10 mils was noted on the edge of the disc. Small globules of eutectic were also observed on each of the discs and in the area of the 5 to 10-mil thicknesses. The eutectic buildup, as well as the globule formation, were, in all probability, due to incomplete draining of the excess eutectic after removal from the final bath.

Sample dimensions were irregular. Thicknesses varied from $5/16$ in. to $3/8$ in., the diameter varying from $1\frac{1}{4}$ in. to $1\frac{5}{16}$ in.

The samples were then exposed to 750F diphenyl for 900 hr. The average weight change (gain) for both discs was $0.5 \text{ mg}/(\text{cm}^2)(\text{mo})$. This was considerably less than weight changes recorded on uncovered uranium specimens tested at the same temperature for approximately the same number of hours. The disc color changed from a dull black, gold-like lustre to a bright copper finish (see Fig. 26; 2.5X magnification). Some peeling of the eutectic was observed under microscopic examination. This peeling occurred on a portion of the disc which had wedged against the side of the autoclave wall. It is quite possible that the coating on the disc may have suffered a deep scratch or was perhaps scored when the specimen was loaded into the autoclave. No other break in the eutectic was noted. The hardness of both the tested and untested samples appeared to be the same under the probing of a fine steel point.

Subsequent samples supplied by ISC showed about the same weight change rate, the same unevenness of coating, but apparently no breaks in the coating. In corrosion tests conducted for 636 hr at 680F, two samples each of copper-9.7% magnesium, and of magnesium-1.4% silicon alloys were also run to test the coating materials. The weight change rates were about +0.5 and +0.1 $\text{mg}/(\text{cm}^2)(\text{mo})$, respectively. The magnesium-silicon eutectic proved to be exceedingly brittle.

On the basis of these preliminary results, continued experimental work on this application technique is also necessary. It is felt that until such time when a metallic coating of one-half to one mil uniform thickness can be assured, a full evaluation of the merits of this type of coating for service in organics is not possible.

UNTESTED

TESTED

FIG. 26
Cu-9.7 WT-% Mg EUTECTIC COATED URANIUM
AFTER 900 HOURS IN 750 F DIPHENYL

APPENDIX A

DETAILED TABULATION OF STATIC CORROSION TESTS

Table VII

STATIC CORROSION TESTS IN 500F DIPHENYL

Sample No.	Material	Test Period	Exposure*, hr	Wt. Change, mg/(cm ²)(mo)	Appearance
A-4413-2	Uranium - 2% Zirconium (Fig. 5)	1	45	+16.0	Loose black coating; autoclave dry.
		2	162	-32.8	Adherent smooth black coating.
		3	787	- 3.72	Slightly loose black coating.
		4	760	- 4.16	Few small pits; loose black coating.
		5	1173	- 1.55	Loose black coating; no change in pitting.
		6	788	- 4.2	Slightly crumbling black coating; no change in pitting
		7	793	- 2.56	Adherent black coating.
A-4413-2A	Uranium - 2% Zirconium (Fig. 5)	1	45	+ 5.72	Loose black coating; autoclave dry.
		2	162	-26.8	Loose black coating.
		3	787	- 4.19	Slightly loose black coating.
		4	760	- 5.86	Loose black coating; linear pit on each end.
		5	1173	- 2.78	Loose black coating; some new small pits.
		6	788	- 4.32	Slightly crumbling black coating; linear pits enlarged.
		7	793	- 5.38	Loose black coating; no change in pitting.
A-4414-1	Uranium (Fig. 3)	1	45	- 1.96	Slightly loose black coating.
		2	162	- 1.36	
		3	787	- 0.982	
		4	760	- 5.36	
		5	1173	- 3.97	Loose, rough black coating.
		6	788	- 3.84	
		7	793	- 5.55	
A-4415-3	Uranium- 5% Zirconium (Fig. 6)	1	45	+ 2.28	Slightly loose black coating.
		2	162	-16.95	Slightly loose dark brown coating.
		3	787	- 2.51	Loose dark brown coating.
		4	760	- 1.4	No change in appearance.
		5	1173	- 2.18	Slightly loose dark brown coating.
		6	788	- 3.02	Adherent black coating; very slight linear pitting.
		7	793	- 2.18	Slightly loose black coating; no change in pitting.
A-4416-4	Uranium- 1.5% Niobium- 5% Zirconium (Fig. 7)	1	45	+ 3.14	Adherent black coating.
		2	162	- 3.30	Slightly loose black coating.
		3	787	- 0.32	Very slightly loose black coating.
		4	760	- 0.058	No change in appearance.
		5	1173	0.000	No change in appearance.
		6	788	+ 0.022	Adherent black coating.
		7	793	- 0.262	No change in appearance.
A-4417-5	Uranium- 2% Molybdenum (Fig. 4)	1	45	-12.2	Loose black coating.
		2	162	- 1.40	
		3	787	- 0.886	
		4	760	- 6.05	
		5	1173	- 1.26	Loose powdery black coating.
		6	788	- 1.88	
		7	793	- 1.18	
A-4418-12	Nickel "A" (Fig. 15)	1	45	- 0.196	No change from original appearance.
		2	162	0.000	
		3	787	+ 0.034	
		4	760	+ 0.017	Tarnish slightly darker.
		5	1173	- 0.008	
		6	788	0.000	
		7	793	- 0.011	Tarnish much darker; brown-black to purple.

* Not cumulative

Table VII (cont'd)

Sample No.	Material	Test Period	Exposure*, Hr	Wt. Change, mg/(cm ²)(mo)	Appearance
A-4419-11	Carbon Steel SAE 1020 (Fig. 13)	1	45	+0.193	Adherent blue tarnish
		2	162	±0.000	Adherent blue-grey tarnish.
		3	787	+0.022	Adherent purple-black tarnish.
		4	760	+0.023	Adherent blue-grey tarnish.
		5	1173	±0.000	Adherent grey-black coating.
		6	788	-0.011	Slight purple cast, one side; otherwise no change.
		7	793	-0.038	Adherent blue tarnish.
A-4424-7	Uranium- 91.8% Alu- minum (Fig. 9)	1	162	+0.055	Original appearance.
		2	787	±0.000	Original appearance.
		3	760	+0.012	Slight grey-black tarnish on one side.
		4	1173	-0.011	No change in appearance.
		5	788	-0.017	
		6	793	-0.017	
A-4425-8	Zircaloy-2	1	162	+0.237	Adherent blue and brown tarnish.
		2	787	+0.027	Adherent dark-grey coating-edges iridescent.
		3	760	±0.000	No change in appearance.
		4	1173	+0.015	Adherent dark-grey coating.
		5	788	-0.022	No change in appearance.
		6	793	+0.016	No change in appearance.
A-4426-9	2S Aluminum (Fig. 10)	1	162	+0.082	Original appearance.
		2	787	+0.011	Autoclave dry; very faint adherent brown tarnish.
		3	760	+0.017	No change in appearance.
		4	1173	±0.000	No change in appearance.
		5	788	±0.000	Tarnish slightly darker.
		6	793	±0.000	No change in appearance.
A-4427-10	Magnesium Dow Pure (Fig. 16)	1	162	+0.560	Adherent grey-brown coating.
		2	787	+0.021	Adherent grey-brown coating.
		3	760	+0.032	No change in appearance.
		4	1173	-0.056	Loose grey-brown coating.
		5	788	-0.042	Adherent grey-brown coating.
		6	793	-0.052	No change in appearance.
A-4427-10A	Magnesium Dow Pure (Fig. 16)	1	162	+0.560	Adherent grey-brown coating.
		2	787	±0.000	Adherent grey-brown coating.
		3	760	+0.043	No change in appearance.
		4	1173	-0.028	Loose grey-brown coating.
		5	788	-0.188	Adherent grey-brown coating.
		6	793	-0.093	No change in appearance.
A-4428-14	Aluminum 99.1%- Nickel 0.9% (Fig. 12)	1	162	+0.082	Original appearance.
		2	787	±0.000	Original appearance.
		3	760	±0.000	No change in appearance.
		4	1173	±0.000	No change in appearance.
		5	788	±0.000	Faint brown tarnish around edges.
		6	793	-0.039	No change in appearance.
A-4429-16	Alcoa Alu- minum Alloy X2219**	1	162	±0.000	Adherent faint brown tarnish.
		2	787	+0.017	Adherent faint brown tarnish.
		3	760	±0.000	No change in appearance.
		4	1173	±0.000	
		5	788	-0.017	
		6	793	-0.033	
A-4430-15	Uranium 9%- Zirconium 88.5%- Tin 2.5% (Fig. 8)	1	162	-0.056	Autoclave lost diphenyl. Original appearance
		2	787	±0.000	Original appearance.
		3	760	+0.024	No change in appearance.
		4	1173	+0.02	Adherent grey-black coating.
		5	788	±0.000	No change in appearance.
		6	793	±0.000	No change in appearance.
A-4431-13	Stainless Steel Type 347 (Fig. 14)	1	162	±0.000	Adherent faint brown tarnish.
		2	787	±0.000	Adherent faint brown tarnish.
		3	760	+0.012	No change in appearance.
		4	1173	+0.007	Adherent light brown tarnish.
		5	788	-0.028	No change in appearance.
		6	793	-0.033	No change in appearance.

* Not cumulative

** Al - 6.2% Cu (Traces Fe, Si, Mn, V, and Zn)

Table VIII
STATIC CORROSION TESTS IN 680F AND 750F DIPHENYL

Test Periods 1 to 5 in 680F Diphenyl
Test Periods 6 and 7 in 750F Diphenyl

Test Period 8 in 750F (527 hr) and
680F (263 hr) Diphenyl

Test Period 9 in 750F Diphenyl

Sample No.	Material	Test Period	Exposure, hr	Wt. Change, mg/(cm ²)(mo)	Appearance
A-4433-1	Uranium	1	187	+ 9.0	Fine loose brown black coating.
		2	379	- 1.99	Loose slightly crumbling black coating.
		3	597	- 0.074	Slight scaling; surface cracking.
		4	1147		SAMPLE DISINTEGRATING.
A-4434-2	Uranium-2% Zirconium (Fig. 5)	1	187	+ 1.145	Fine, loose, reddish black coating.
		2	379	- 5.2	Loose, reddish-black coating.
		3	579	- 5.06	Loose, slightly crumbling black coating.
		4	1147	- 4.72	Loose, crumbling black coating.
		5	784	- 1.8	Loose, crumbling black coating.
		6	762	- 6.3	Slightly loose, crumbling black coating.
		7	862	- 3.58	No change in appearance.
		8	790	- 4.59	Very slight pitting; otherwise no change in appearance.
		9	1411	- 1.81	No change in appearance.
A-4434-2A	Uranium-2% Zirconium (Fig. 5)	1	187	- 2.75	Fine loose reddish-black coating.
		2	379	- 8.16	Loose, slightly crumbling brown coating.
		3	597	-12.97	Loose crumbling black coating.
		4	1147	- 3.48	
		5	784	- 3.19	
		6	762	- 8.91	Slightly loose, crumbling coating.
		7	862	- 4.83	No change in appearance.
		8	790	- 6.31	Slight linear pitting; no other change.
		9	1411	- 2.44	No change in appearance.
A-4435-3	Uranium-5% Zirconium (Fig. 6)	1	187	- 0.43	Fine moderately loose brown coating.
		2	379	+ 0.082	Loose, slightly crumbling brown-black coating.
		3	597	- 2.28	Loose, brown-black coating.
		4	1147	- 0.935	Autoclave lost diphenyl; loose powdery black coating.
		5	784	- 1.77	Loose powdery black coating.
		6	762	- 3.81	Autoclave dry; adherent black coating.
		7	862	- 1.19	Slightly loose, black coating.
		8	790	- 1.71	Adherent black-coating.
		9	1411	- 0.412	1/2 volume of diphenyl lost; slightly loose powdery black coating.
A-4436-4	Uranium-5% Zirconium-1.5% Niobium (Fig. 7)	1	187	- 0.944	Very slight black coating.
		2	379	- 0.07	Loose, slightly crumbling, black coating.
		3	597	- 0.992	Loose black coating.
		4	1147	- 0.682	Autoclave lost diphenyl; loose powdery black coating.
		5	784	- 1.18	Loose powdery black coating.
		6	762	- 1.38	Autoclave dry; adherent black coating.
		7	862	- 1.49	Slightly loose black coating.
		8	790	- 3.66	Adherent black coating.
		9	1411	+ 1.03	No change in appearance; autoclave lost diphenyl.
A-4437-5	Uranium-2% Molybdenum	1	187	- 1.632	Fine loose black coating.
		2	379	- 7.74	Loose black coating.
		3	597	- 2.45	Loose black coating.
		4	1147	+ 3.91	Cracked around edges. Surface blistering.
		5	784	-	Laminar crumbling; surface disintegrating.
A-4438-7	Uranium-91.8% Aluminum (Fig. 9)	1	187	- 0.048	No change in appearance.
		2	379	- 0.059	
		3	597	- 0.015	
		4	1147	- 0.043	
		5	784	- 0.011	
		6	762	+ 0.011	Test concluded.
		7	862	+ 0.01	
A-4439-8	Zircaloy 2	1	187	+ 0.680	Dull light green coating.
		2	379	+ 0.056	Dull, grey-black coating.
		3	597	+ 0.129	
		4	1147	+ 0.011	
		5	784	+ 0.544	Slightly loose, grey coating.
		6	762	+ 0.66	Adherent grey-black coating.
		7	862	+ 0.025	Test concluded. Sample sent to KAPL for analysis.

Table VIII (Cont'd.)

Sample No.	Material	Test Period	Exposure, hr	Wt. Change, mg/(cm ²)(mo)	Appearance
A-4440-9	2S Aluminum (Fig. 10)	1	187	± 0.000	No change in appearance
		2	379	- 0.058	Very slight brown tarnish.
		3	597	+ 0.037	Tarnish slightly darker; small black spots on one edge.
		4	1147	- 0.054	No change in appearance.
		5	784	- 0.017	No change in appearance.
		6	762	± 0.000	Sample has greyish cast.
		7	862	± 0.000	No change in appearance. Test concluded.
A-4441-10	Magnesium Dow Pure (Fig. 16)	1	187	+ 0.453	Adherent dark grey tarnish on ends; original appearance in center.
		2	379	+ 0.727	Adherent brown coating.
		3	597	+ 0.454	Adherent, dark brown coating.
		4	1147	- 1.180	Brown coating; loose and flaked off.
		5	784	- 0.663	Black coating over loose flaking brown coating; adherent grey coating underneath.
		6	762	- 0.96	Large spot of loose black coating on both sides.
		7	862	- 0.707	Loose flaky grey-black coating. Test concluded.
A-4442-11	Carbon Steel SAE 1020 (Fig. 13)	1	187	+ 0.882	Slight, loose, black coating over blue-black finish.
		2	379	+ 0.195	Adherent black coating.
		3	597	+ 0.073	
		4	1147	- 0.015	
		5	784	+ 0.180	
		6	762	+ 0.168	No change in appearance. Test concluded.
		7	862	+ 0.091	
A-4443-12	Nickel "A" (Fig. 15)	1	187	- 0.028	Faint grey scorch-like appearance on ends.
		2	379	- 0.023	Slight grey-black tarnish; darker at ends.
		3	597	+ 0.014	Tarnish slightly darker.
		4	1147	- 0.056	
		5	784	+ 0.033	
		6	762	+ 0.005	
		7	862	+ 0.010	No change in appearance. Test concluded.
A-4444-13	Stainless Steel Type 347 (Fig. 14)	1	187	± 0.000	No change in appearance.
		2	379	- 0.046	Grey brown tarnish
		3	597	± 0.000	Tarnish slightly darker.
		4	1147	- 0.061	Adherent brown tarnish.
		5	784	± 0.000	Tarnish slightly darker.
		6	762	± 0.000	Adherent dark brown, purple tarnish.
		7	862	+ 0.010	Adherent dark, brown, blue and purple tarnish. Test concluded.
A-4445-14	Aluminum 99.1% Nickel 0.9% (Fig. 12)	1	187	+ 0.000	No change in appearance.
		2	379	- 0.035	
		3	597	± 0.000	
		4	1147	- 0.047	
		5	784	- 0.040	Surface slightly duller. Otherwise no change in appearance.
		6	762	+ 0.018	
		7	862	± 0.000	No change in appearance. Test concluded.
A-4446-15	Uranium 9%-Zirconium 88.5%-Tin 2.5% (Fig. 8)	1	187	+ 1.080	No change in appearance.
		2	379	+ 0.776	
		3	597	+ 0.372	
		4	1147	- 0.312	Loose grey-brown coating.
		5	784	- 0.792	Slightly loose grey-brown coating.
		6	762	- 4.410	No change in appearance.
		7	862	- 4.64	Loose powdery grey-black coating.
		8	790	- 1.73	Slightly loose grey-black coating.
		9	1411	- 1.35	Loose powdery grey-black coating.
A-4447-16	Alcoa Aluminum Alloy (X2214) (Fig. 11)	1	187	+ 0.073	No change in appearance.
		2	379	± 0.000	Very slight grey-brown tarnish.
		3	597	+ 0.044	Tarnish slightly darker on back side.
		4	1147	- 0.035	
		5	784	- 0.056	
		6	762	- 0.005	
		7	862	± 0.000	No change in appearance. Test concluded.

Table IX

SUPPLEMENTARY STATIC CORROSION TESTS IN 750F AND 680F DIPHENYL

Test Periods 1 and 2 in 750F Diphenyl
 Test Period 3 in 680F (263 hr) and 750F (527 hr) Diphenyl
 Test Period 4 in 750F Diphenyl

Sample No.	Material	Test Period	Exposure, hr	Wt. Change, mg/(cm ²)(mo)	Appearance
A-4545-1B	Uranium (Fig. 3)	1	762	+ 0.779	Adherent black coating.
		2	862	- 2.95	Slightly loose black coating.
		3	790	- 7.12	No change in appearance.
		4	1411	- 1.93	No change in appearance.
A-4547-1A	Uranium* (Fig. 3)	1	762	+ 0.801	Adherent black coating.
		2	862	- 4.26	Slightly loose black coating.
		3	790	- 5.12	No change in appearance.
		4	1411	- 1.65	Loose powdery black coating.
A-4546-5B	Uranium-2% Molybdenum (Fig. 4)	1	762	- 0.147	Loose slightly crumbling black coating.
		2	862	- 2.14	No change in appearance.
		3	790	- 3.88	
		4	1411	- 1.80	
A-4548-5A	Uranium-2% Molybdenum* (Fig. 4)	1	762	+ 0.025	Loose slightly crumbling black coating.
		2	862	- 3.71	No change in appearance.
		3	790	- 3.41	Slightly loose black coating.
		4	1411	- 1.32	Loose black coating.
A-4550-8A	Zircaloy 2 (Fig. 20)	1	762	+ 0.325	Adherent black coating.
		2	862	+ 0.332	No change in appearance.
		3	790	+ 0.248	Adherent dark grey coating.
		4	1411	+ 0.169	Adherent grey-black coating.
A-4549-16A	Alcoa Aluminum Alloy X2219 (Fig. 11)	1	762	+ 0.012	Very faint adherent tarnish on back side; other sides have original appearance.
		2	862	+ 0.000	No change in appearance.
		3	790	+ 0.000	No change in appearance.
		4	1411	+ 0.013	Faint adherent tarnish on front side; tarnish on back side slightly darker.

* Diphenyl vapors deliberately ignited and allowed to burn for a few seconds before they were extinguished and the autoclave sealed.

41

Table X
STATIC CORROSION TESTS ON CONTROL ROD MATERIALS IN 500F DIPHENYL

Sample No.	Material	Test Period	Exposure, hr	Wt. Change, mg/(cm ²)(mo)	Appearance
A-4551	1.2% Boron-Steel (pickled) (Fig. 18)	1	793	- 0.011	Adherent light grey brown tarnish.
		2	743	- 0.012	
		3	1098	+ 0.020	No change in appearance.
		4	1001	+ 0.013	
A-4552	2.02% Boron-Steel (pickled) (Fig. 18)	1	793	± 0.000	Adherent grey tarnish.
		2	743	- 0.012	No change in appearance.
		3	1098	± 0.000	Adherent grey-black tarnish.
		4	1001	± 0.000	No change in appearance.
A-4553	Cadmium 30%-Silver 70% (Fig. 17)	1	793	+ 0.010	Slightly loose gold-brown coating.
		2	743	- 0.083	No change in appearance.
		3	1098	- 0.045	No change in appearance.
		4	1001	- 0.012	Slightly loose greenish-brown coating.
A-4554	2.18% Boron-Steel (Fig. 18)	1	793	± 0.000	Sample has original appearance.
		2	743	- 0.017	No change in appearance.
		3	1098	- 0.012	Sample getting darker from a slight tarnish.
		4	1001	± 0.000	No change in appearance.
A-4555	0.97% Boron-Steel (Fig. 18)	1	793	+ 0.011	Sample has original appearance.
		2	743	- 0.018	No change in appearance.
		3	1098	- 0.012	Sample has slight grey-brown tarnish.
		4	1001	+ 0.009	No change in appearance.
A-4556	Graphitars: No. 14, 38, 30, and 41				Samples No. 14 and 38, (non-porous) and samples No. 30 and 41 (porous), show no physical change after 3635 hours in 500F diphenyl. Physical properties of these grades are given in the following tabulation.

Graphitar Grade No.	Average Scleroscope Hardness*	Average Apparent Density	Average Transverse Breaking Strength, psi	Average Compressive Strength, psi	Friction 1 - Low 2 - Low-Medium 3 - Medium
14	100 (70)	1.7	11,000	35,000	1
30	75 (56)	1.7	10,000	18,000	1
38	85 (62)	1.7	11,000	35,000	1
41	85 (62)	1.7	11,000	33,000	2

* Value in parenthesis is corresponding Rockwell C Hardness

From the starting materials of graphite and pitch binder, the initial baking operations at 3000F or higher form the porous grades, presumably converting the binder completely to carbons. The porous grade may be impregnated with resin and usually is baked at 400F. A given non-porous grade may be the result of several impregnations and bakings. Non-porous grades are generally stronger and harder, and are used for any bearings and pressure seals. The porous grades find greatest application in lubricated bearings.

Table XI

STATIC CORROSION TESTS IN 500F DIPHENYL WITH 500 psi NITROGEN

Sample	Material	Test Period	Exposure, hr	Wt. Change, mg/(cm ²)(mo)	Appearance
A-4585	Zircaloy 2 (Fig. 20)	1	337	+ 0.088	Adherent greyish-purple tarnish; green to straw color on edges.
		2	382	+ 0.112	Adherent black coating. Green to blue tarnish on edges.
		3	646	+ 0.033	Adherent black coating. Dark red and green tarnish on edges.
		4	1001	+ 0.034	Adherent black coating. Dark green tarnish on edges.
A-4586	Aluminum 2S (Fig. 10)	1	337	+ 0.0	Few black specks on edges; otherwise original appearance.
		2	382	+ 0.023	No change in appearance.
		3	646	+ 0.021	Adherent faint straw tarnish.
		4	1001	+ 0.0	No change in appearance.
A-4587	Magnesium Dow Pure (Fig. 16)	1	337	- 0.053	Adherent thin grey-tarnish.
		2	382	+ 0.07	Adherent grey-brown tarnish.
		3	646	+ 0.048	No change in appearance.
		4	1001	+ 0.20	Adherent brown coating. Sample slightly warped.
A-4584-2	Uranium-2% Zirconium	1	337		Sample Disintegrated
A-4584-2A	Uranium-2% Zirconium	1	337		Sample Disintegrated
A-4596	Uranium-91.8% Aluminum minimum (Fig. 9)	1	382	- 0.025	Sample has original appearance.
		2	646	- 0.015	Faint grey tarnish on one side.
		3	1001	+ 0.019	No change in appearance.

43

Table XII
STATIC CORROSION TESTS ON ZIRCONIUM AND ZIRCONIUM ALLOYS
IN 750F AND 680F DIPHENYL

Test Period 1: 750F (331-377 hr); 680F (263 hr)
Test Period 2: 750F Diphenyl

Sample No.	Material	Test Period	Exposure, hr	Wt. Change, mg/(cm ²)(mo)	Appearance
A-4597-A	Zirconium Sponge (Fig. 19)	1	640	+ 0.240	Adherent grey-black coating.
		2	1411	+ 0.071	No change in appearance.
A-4597-B	Zirconium Sponge (Fig. 19)	1	640	+ 0.168	Adherent grey-black coating.
		2	1411	+ 0.011	No change in appearance.
A-4598-A	Zirconium Grade III (Fig. 19)	1	640	+ 0.317	Adherent lustrous black tarnish.
		2	1411	+ 0.237	Adherent lustrous grey-black tarnish.
A-4598-B	Zirconium Grade III (Fig. 19)	1	640	+ 0.349	Adherent lustrous black tarnish.
		2	1411	+ 0.280	Adherent lustrous grey-black tarnish.
A-4599-A	Zirconium Grade I (Fig. 19)	1	640	+ 0.539	Adherent semi-lustrous grey-black tarnish.
		2	1411	+ 0.294	No change in appearance.
A-4599-B	Zirconium Grade I (Fig. 19)	1	640	+ 0.460	Adherent semi-lustrous grey-black tarnish.
		2	1411	+ 0.302	No change in appearance.
A-4600-A	Zircaloy 2 (Fig. 20)	1	640	+ 0.202	Adherent lustrous grey-black tarnish.
		2	1411	+ 0.100	Adherent black tarnish.
A-4600-B	Zircaloy 2 (Fig. 20)	1	640	+ 0.189	Adherent lustrous grey-black tarnish.
		2	1411	+ 0.109	Adherent black tarnish.
A-4601-A	Zircaloy 3 (Fig. 21)	1	640	+ 0.329	Adherent grey-black coating with thin grey streaks.
		2	1411	+ 0.131	No change in appearance.
A-4601-B	Zircaloy 3 (Fig. 21)	1	640	+ 0.323	Adherent grey-black coating with thin grey streaks.
		2	1411	+ 0.075	No change in appearance.
A-4602-C	Zircaloy 3 (pickled) (Fig. 21)	1	594	+ 0.044	Adherent dark multicolored tarnish, thin grey streaks.
		2	1411	+ 0.078	Tarnish almost black; otherwise no change in appearance.
A-4602-D	Zircaloy 3 (pickled) (Fig. 21)	1	594	+ 0.037	Adherent dark multicolored tarnish; thin grey streaks.
		2	1411	+ 0.065	Tarnish almost black; otherwise no change in appearance.
A-4603-C	Zircaloy 2 (pickled) (Fig. 20)	1	594	+ 0.067	Adherent lustrous dark red and green to black tarnish.
		2	1411	+ 0.105	No change in appearance.
A-4603-D	Zircaloy 2 (pickled) (Fig. 20)	1	594	+ 0.054	Adherent lustrous dark red and green to black tarnish.
		2	1411	+ 0.085	No change in appearance.