Corrosion of Stainless Steel and Aluminum Alloys in Fuming Nitric Acid - II

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I. INTRODUCTION

This is the second report of an investigation prompted by corrosion problems which arose in rocket motor test installations during the course of propulsion research under USAF Contract W-33-038-ac-14222. The results of the laboratory corrosion tests with white fuming nitric acid (WFNA) described herein supplement those with red fuming nitric acid (RFNA) described in the previous report (Ref. 1). The tests were designed to give qualitative answers to specific questions and were made as simple as possible. Numerous shortcomings of the tests are fully recognized. The results are not claimed to be generally applicable and should be used with caution; however, it is believed that useful information is furnished about trends in the corrosion rates of various stainless steel and aluminum alloys with time, and about their relative corrosion resistance under various specified test conditions.

The earlier report included a brief discussion of various factors involved in corrosion and its measurement, as well as a critical summary of corrosion data for stainless steel and aluminum alloys in fuming nitric acids. These data were selected from the chemical literature, from classified reports, and from private communications with steel and aluminum companies. The only additional data to come to the attention of the authors were presented at the Symposium on the Practical Factors Affecting the Application of Nitric Acid and Mixed Oxides of Nitrogen as Liquid Rocket Oxidizers, sponsored by the Committee on Fuels and Lubricants of the Research and Development Board on October 10-12, 1951. These data will be available in the printed transcript of the symposium (Ref. 2).

Examination of the literature reveals little effective coordination of testing programs among laboratories which have common corrosion problems with fuming nitric acids. Moreover, the results of many incidental laboratory corrosion tests are never published, or reach print obscurely in general progress reports or in appendices to reports on other subjects. In spite of the probable duplication of effort, it is difficult to compare the results of different investigators. The numerous factors involved in corrosion and its measurement are often given inadequate consideration, indicating that the limited applicability of the results of laboratory tests is not always appreciated. The most obvious example is the popularity of corrosion tests of a few days duration, the results of which are extrapolated to predict corrosion rates for periods of months or years. Another example is failure to consider the possibility of galvanic corrosion when two dissimilar alloys are coupled in fuming nitric acid; the extent of this type of corrosion cannot be predicted on the basis of the corrosion rates of the isolated alloys.

A comprehensive, well-planned, carefully controlled, and properly interpreted laboratory and field corrosion testing program is urgently needed. The test specimens should be exposed to the corrosive conditions for a sufficiently long time to furnish adequate and reliable data concerning the corrosion of stainless steel and aluminum alloys by fuming nitric acids.

II. SUMMARY AND CONCLUSIONS

Laboratory corrosion tests of types 303 (cold-rolled), 316 (cold-rolled), and 347 (forged billet) stainless steels, and of types 2S-0, 3S-0, 17S-T, and 24S-T aluminum alloys in WFNA were conducted for a period of three months. In four series of tests corrosion rates were determined for each alloy under the following conditions, designed to duplicate those encountered at the rocket test facility: I. Continuous exposure to commercial 98% WFNA; II. Continuous exposure to both WFNA and its vapor; III. Alternate exposure to WFNA and to dilute acid; IV. Alternate exposure to WFNA and to the atmosphere. In a fifth series, the samples were exposed continuously to 6.5% RFNA. This series duplicated one reported previously (Ref. 1) and served to check the reproducibility of the earlier results as well as to furnish a basis for comparing the two sets of tests.

The results of these experiments with WFNA and those with RFNA reported earlier (Ref. 1), together with the best data available in the literature, lead to the following conclusions:

1. Aluminum alloys are definitely superior to stainless steels for long term continuous exposure or for intermittent exposure at room temperature to fuming nitric acid and its vapor. The corrosion rates of aluminum alloys in fuming nitric acid remain fairly constant with time, while those for some stainless steels increase.

2. The aluminum alloys 2S-0, 3S-0, 17S-T, and 24S-T are practically equivalent in their resistance to fuming nitric acids.

3. Aluminum alloys are readily attacked by dilute nitric acid; hence, they should never be exposed to such attack for any appreciable time, e. g., by draining of fuming nitric acid and leaving in water or air without very thorough rinsing.

4. Of the stainless steels tested, type 347 was most resistant to corrosion by fuming nitric acid. Based upon data available in the literature, low-carbon 304 is comparable to 347 in corrosion resistance. The low-carbon 304 stainless is recommended (Ref. 3) as the better choice in view of current restrictions on columbium needed for 347.

5. Stainless steel for which only intermittent contact with fuming nitric acid is required should be drained and rinsed between exposures.

6. WFNA is roughly two to five times as corrosive as RFNA to stainless steels. Corrosion rates of aluminum alloys are somewhat lower in WFNA than in RFNA.

III. EXPERIMENTAL

A. Alloys Investigated

Stainless steel types 303, 316, and 347, and aluminum alloys 2S-0, 3S-0, 17S-T and 24S-T were studied. The 347 sample was cut from a forged billet, while the 303 and 316 were from cold-rolled stock. Samples of 303 and 316 and of 17S-T and 24S-T were cut from round bar stock and given a smooth machine finish. Samples of 2S-0 and 3S-0 were cut from 1/8 inch sheet and received no surface treatment. The samples of each alloy were cut from the same stock as the samples used earlier in tests with RFNA (Ref. 1).

B. Testing Procedures

Five series of tests were conducted as described below for a period of three months. Series I and II simulated conditions in drums or other containers totally or partially filled with WFNA. The cycles in Series III and IV were designed to show whether parts of the rocket motor facility which must be exposed intermittently to WFNA should be left in air or in water, after draining and rinsing, during the periods between exposures to acid. Series I(a) was a control run in RFNA.

Series I: The samples were immersed completely in WFNA.

Series II: Approximately half the surface area of each sample was immersed in WFNA, the remainder being exposed to the acid vapor. After removal for weighing, each sample was replaced in such a way that the same portion was immersed in acid.

Series III: The samples were immersed in WFNA during the first phase of each cycle. After weighing, the samples were immersed momentarily in WFNA, dipped quickly into water, and all placed together, but not touching each other, in 100 ml. of water (actually dilute acid because of incomplete rinsing of samples). The samples were reweighed at the end of each phase. Seventeen cycles involving phase times of two to five days were completed.

Series IV: The samples were immersed in WFNA during the first phase of each cycle. After weighing, the samples were redipped in WFNA, incompletely rinsed by a quick dip in water, and left in air. Seventeen cycles were completed.

Series I(a): RFNA (6.5%) was used in this series under the same conditions as for Series I. The reason for this was to check reproducibility of results previously reported (Ref. 1) and to furnish a better basis for comparing the two sets of tests.

At the beginning of the test the samples, measuring 1/2" x 1/2" x 1/8", were washed with acetone, dried and weighed. One sample of each of the seven alloys was included in each of the five test series, with the exception of Series II for which no 316 sample was available. All samples of a given series were placed on edge, continuously or at intervals, in 100 ml. of acid in a 250 ml. glass-stoppered Erlenmeyer flask, care being taken that the samples did not touch each other. Only 30 ml. of acid was used in Series II. The acid, which was commercial 6.5% RFNA for Series I(a) and commercial 98% WFNA for all others, was changed at weekly intervals. The RFNA available for Series I(a) after the first two months was from a different batch known to be old and badly contaminated. For this reason, although the tests were continued for three months, all calculations for I(a) were based on the first two-month period.

The temperatures at which the experiments were performed were the prevailing temperatures in the laboratory, varying from 65° to 90° F. and averaging about 75° F.

Weight losses of the samples were determined at intervals of two to five days. Each sample was rinsed quickly and thoroughly with water, dried with a towel, and rubbed with a chamois to remove lint before weighing. When the weight loss of a sample amounted to 50%, the test on the sample was discontinued.

C. Experimental Results

1. Physical Appearance of Test Samples

Series I: The steel samples had started to blacken after one day in WFNA, and at the end of six days all three samples were covered with a shiny black film. After eighteen and twenty-eight days, respectively, the samples of 316 and 303 were badly attacked, i.e., had rough and pitted surfaces. After thirty-five days the weight loss of the 316 sample amounted to over 50%; hence, the test on this sample was discontinued. The test on the 303 sample was discontinued after seventy-four days for the same reason. The 347 sample lost 18% of its weight during the ninety days of the test.

After three days in WFNA the aluminum samples 17S-T and 24S-T bore vari-colored tarnishes, the colors changing and darkening with time until after three months they were a dull grey. The 2S-0 and 3S-0 samples were only slightly dulled after ninety days.

Series II: After three days exposure to WFNA and its vapor, each steel sample had darkened slightly and uniformly, and three days later all were black. The surface of the 303 sample was rough after thirty days. The 347 sample was not badly attacked after ninety days. No 316 sample was available for this series.

The aluminum samples bore vari-colored tarnishes after one day. At the end of three months, the 2S-0 and 3S-0 were dulled, while the 17S-T and 24S-T were black where immersed in the liquid and gray on the parts exposed to the vapor. Slight pitting occurred.

No preferential attack at liquid-vapor interfaces was apparent on either the steel or aluminum samples.

Series III: The steel samples were still clean after one cycle, but started to darken after the second exposure to WFNA and were completely black after the third exposure to the acid. The 316 sample deteriorated so rapidly that the test on it was discontinued after fifty-eight days, including thirty days of exposure to WFNA.

As in all the other series, the aluminum samples were tarnished after one day in WFNA. The tarnish varied thereafter, being grayish after the water phases and brightly colored after the acid phases.

Series IV: The appearance of both the steel and aluminum samples was essentially the same as in Series III. The 316 sample was removed from the test after fifty-eight days. In many cases, the tarnish on the aluminum samples lightened during exposure to air and darkened again in acid.

Series I(a): All the stainless steel samples had shiny black finishes after eighteen days in RFNA. The 316 and 303 samples were very rough after twenty-eight and fifty days respectively, and the 316 sample was removed from the test after fifty-six days.

The aluminum samples were tarnished after one day in RFNA, the colors changing and darkening with time. Slight pitting was apparent at the end of the test.

The appearance of all the steel and aluminum samples at the beginning and at the end of the test period is shown in Figure 13.

2. Calculations

Average corrosion rates in inches per month (ipm) were calculated for the samples in Series I and II for the three months period, and for the samples of Series I(a) for a two month period. Average corrosion rates over the three months period were calculated for each phase of the testing cycle for samples in Series III and IV. These rates are tabulated in Figure 14. Corrosion rates in ipm calculated for the intervals between weighings are plotted vs. elapsed time for the five series in Figures 1 through 10.

3. Comparison of Alloys Tested; Effect of Test Conditions

a. Steels: The 303, 316, and 347 stainless steel samples showed no significant differences in corrosion resistance for about the first two weeks. Thereafter until the conclusion of three months testing, the 316 samples were attacked most rapidly under all test conditions, and the 347 samples were attacked most slowly. Samples of each steel exhibited slightly smaller over-all corrosion rates when exposed simultaneously to both liquid WFNA and its vapor (Series II) than when exposed to liquid WFNA alone (Series I).

The over-all corrosion rates of the steel samples during the WFNA phases of the cycling tests were of the same order of magnitude as those of samples exposed continuously to WFNA. Corrosion rates in the alternate phases, i.e., water after rinsing in Series III, and air after rinsing in Series IV, were much smaller than in WFNA. No significant difference between the cycles WFNA-rinse-water and WFNA-rinse-air was observed for the steel samples.

b. Aluminum alloys: The 2S-0, 3S-0, 17S-T, and 24S-T alloys investigated were decidedly superior to the stainless steels in their resistance to WFNA and its vapor, as shown by the representative corrosion-rate curves in Figure 11.

The average corrosion rate of type 347, the best stainless steel tested, was about ten times as great as the corrosion rates of any of the aluminum alloys in Series I. The overall corrosion rates of aluminum samples exposed simultaneously to both liquid and vapor were lower than those of samples exposed to liquid WFNA alone. Differences among the four alloys in the various tests were small, the 17S-T being slightly more resistant to liquid WFNA than the others.

When the aluminum alloy samples were taken from WFNA, rinsed, and left in water or air, their corrosion rates increased. This was to be expected, since it is well known that aluminum is attacked by dilute nitric acid.

In Series IV a growth of white crystals was formed on the aluminum samples during the air phases. These crystals were often not noticeable until disturbed by brisk rubbing. The results for this series indicate the possibility that some of these crystals were overlooked in cleaning the samples and were later dissolved in the acid phases. This may be the reason that the apparent corrosion rates are higher in the acid phases and lower in the air phases than would be expected on the basis of the other series.

4. Comparison of Corrosion by WFNA and RFNA

The average corrosion rates for the tests in WFNA are tabulated in Figure 14, and the corresponding values for the earlier tests in RFNA are tabulated in Figure 15. Figure 14 also contains the results of the control Series I(a), which was run in RFNA simultaneously with the WFNA tests. The corrosion rates observed in Series I(a), compared with the rates for the duplicated Series I (Fig. 15), are smaller by about 50% for the 303 and 347 stainless steels, about equal for 316 stainless, and about 25% larger for the aluminum alloys. It must be kept in mind that the test periods were two months and three months for the respective series. Some idea of the degree of reproducibility of the measured corrosion rates is thus obtained.

Direct comparison of the rates given in Figures 14 and 15 leads to the following generalities concerning the relative corrosivity of 98% WFNA and 6.5% RFNA.

In Series I, III, and IV, corrosion rates of 303 and 347 stainless steels were roughly twice as great in WFNA as in RFNA, while in Series II the rates were about five times as great in WFNA. The 316 samples were also more severly attacked by the WFNA, as shown by their higher corrosion rates in tests which had to be discontinued sooner than those in RFNA.

For the aluminum alloys, corrosion rates were higher in RFNA than in WFNA for the samples in Series I by a factor of about 1.1, and in Series II and III by a factor of about 1.7. In Series IV WFNA appeared to attack the 17S-T and 24S-T aluminum alloys more severely than did RFNA. However, the data in Series IV in WFNA lacks the consistency of the other data. This may be due in part to suspected experimental errors described in paragraph 3 above.

5. Effect of Temperature and Acid Renewal on Steels

Some of the irregularities in the curves of Figure 1, which show corrosion rates vs. time for the steels of Series I, may be explained on the basis of information contained in Figure 12. The curve for 347 steel is reproduced from Figure 1, and a temperature plot is superimposed. The temperatures are those recorded at the same time each day and give a fair indication of the over-all temperature fluctuations during the test. The points at which the acid was changed are circled in the corrosion-rate plot. There appears to be little correlation between corrosion rate and temperature fluctuation, but the corrosion rate increased sharply after each acid change. The one point, at sixty days, when the acid change did not produce a large increase in corrosion rate occurred after the clean dry sample had been left in air for five days awaiting the arrival of fresh acid.

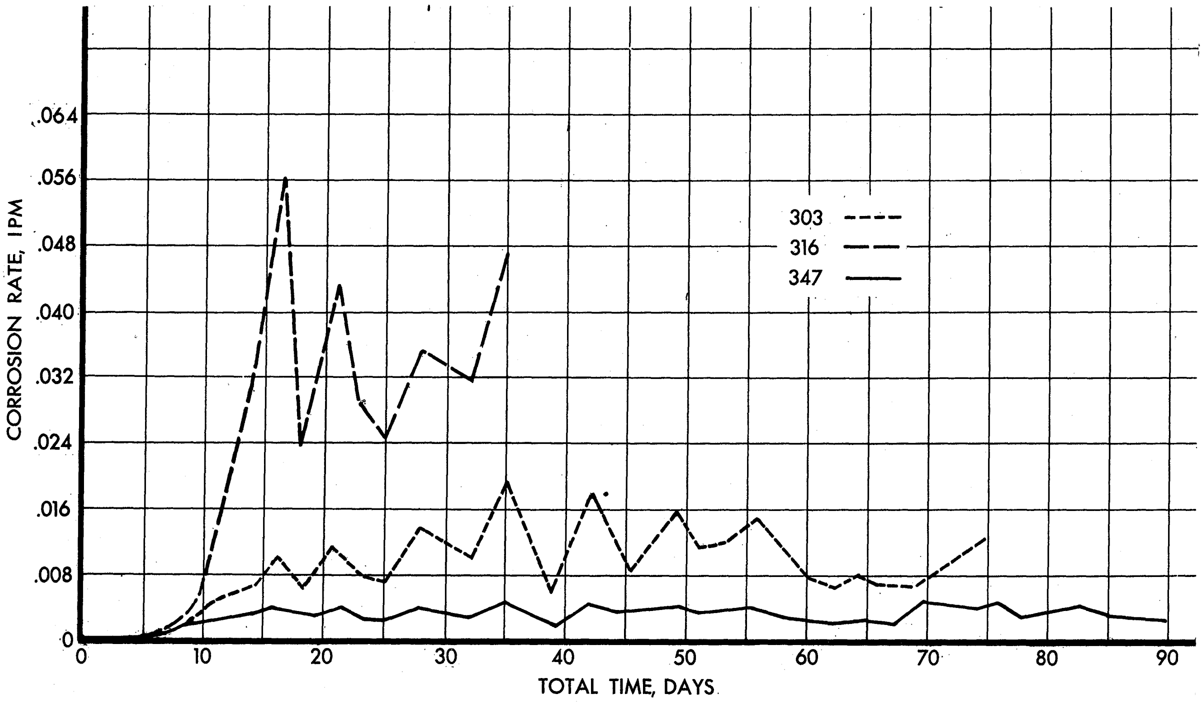

FIG. 1 SERIES I: CORROSION OF STAINLESS STEELS
Continuous Exposure to WFNA

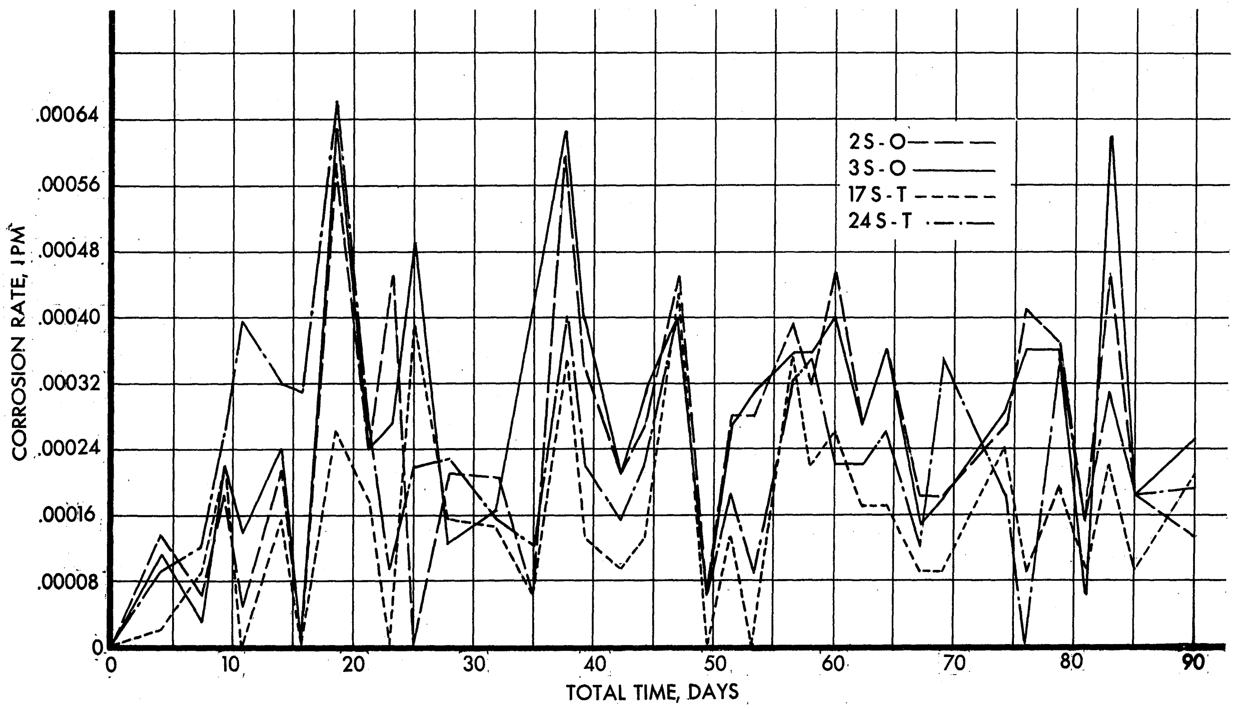

FIG. 2 SERIES I: CORROSION OF ALUMINUM ALLOYS
Continuous exposure to WFNA

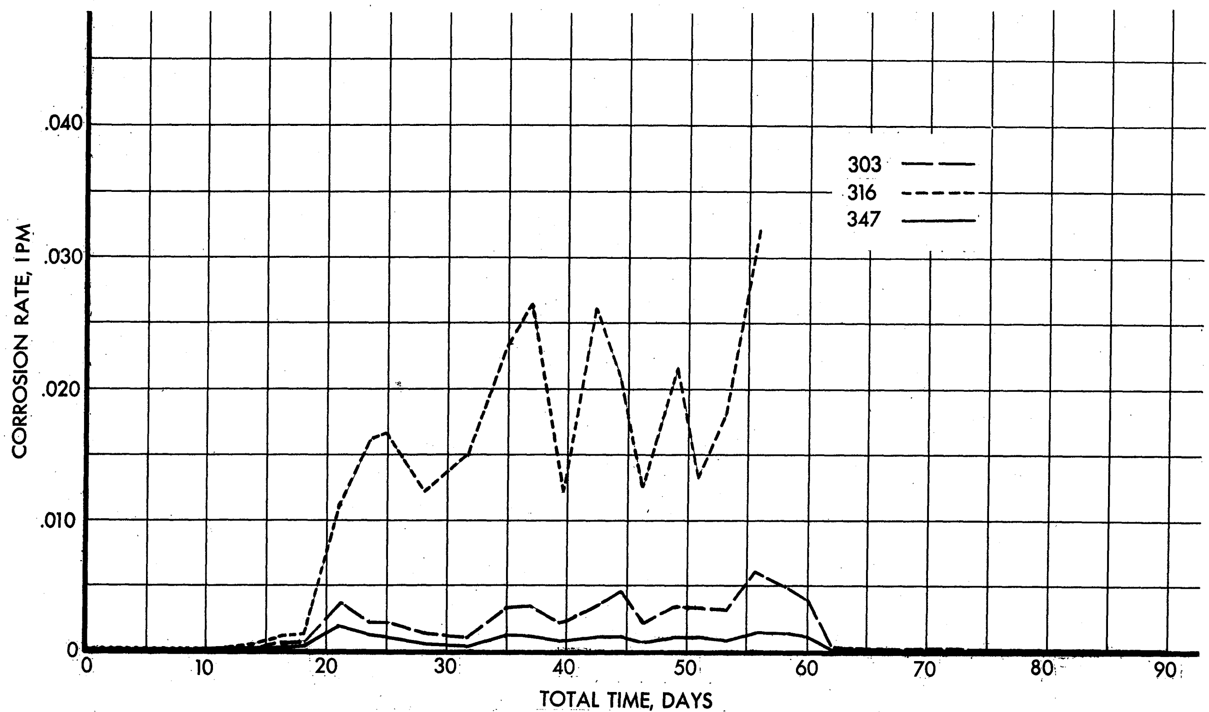

FIG. 3 SERIES I(a): CORROSION OF STAINLESS STEELS
Continuous exposure to 6.5% RFNA

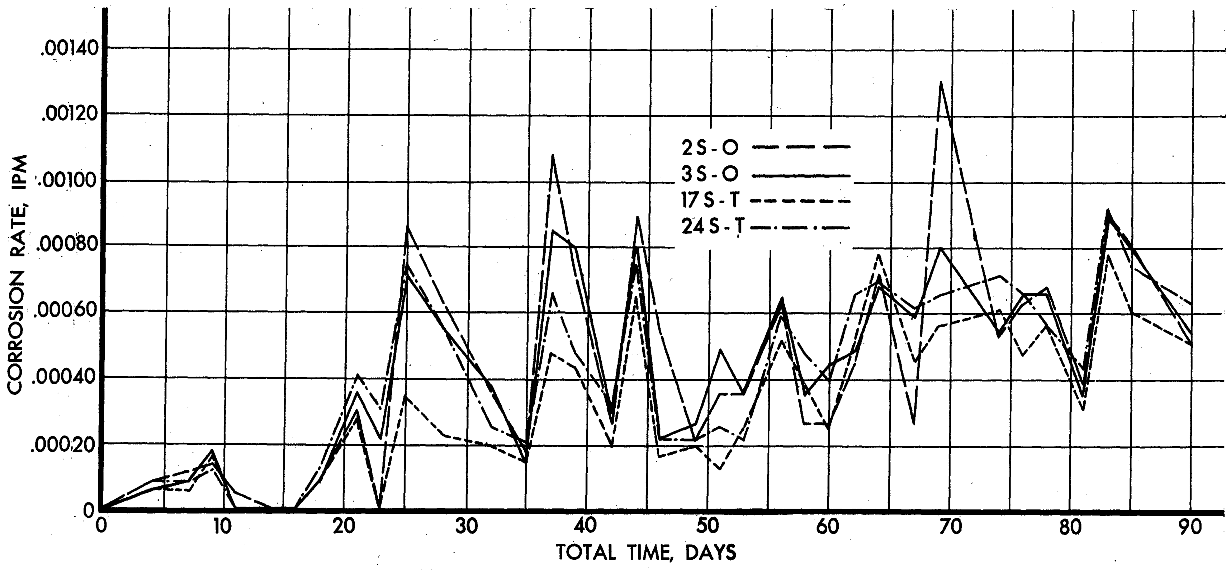

FIG. 4 SERIES I (a): CORROSION OF ALUMINUM ALLOYS
Continuous exposure to 6.5% RFNA

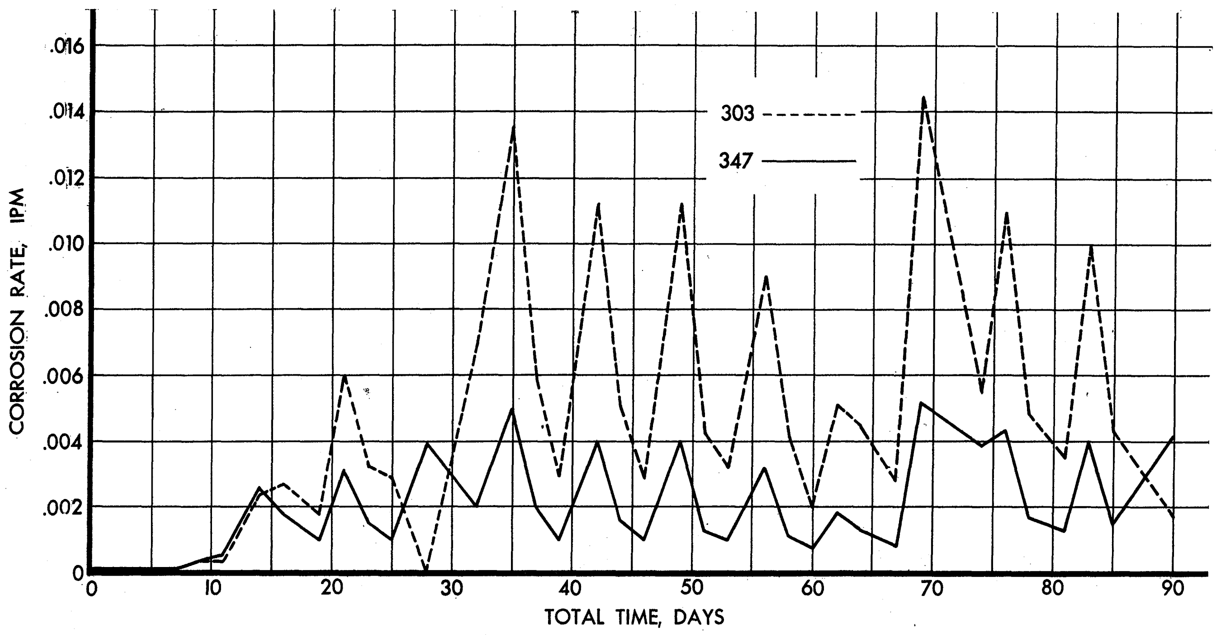

FIG. 5 SERIES II: CORROSION OF STAINLESS STEELS
Continuous exposure to both liquid and fumes of WFNA

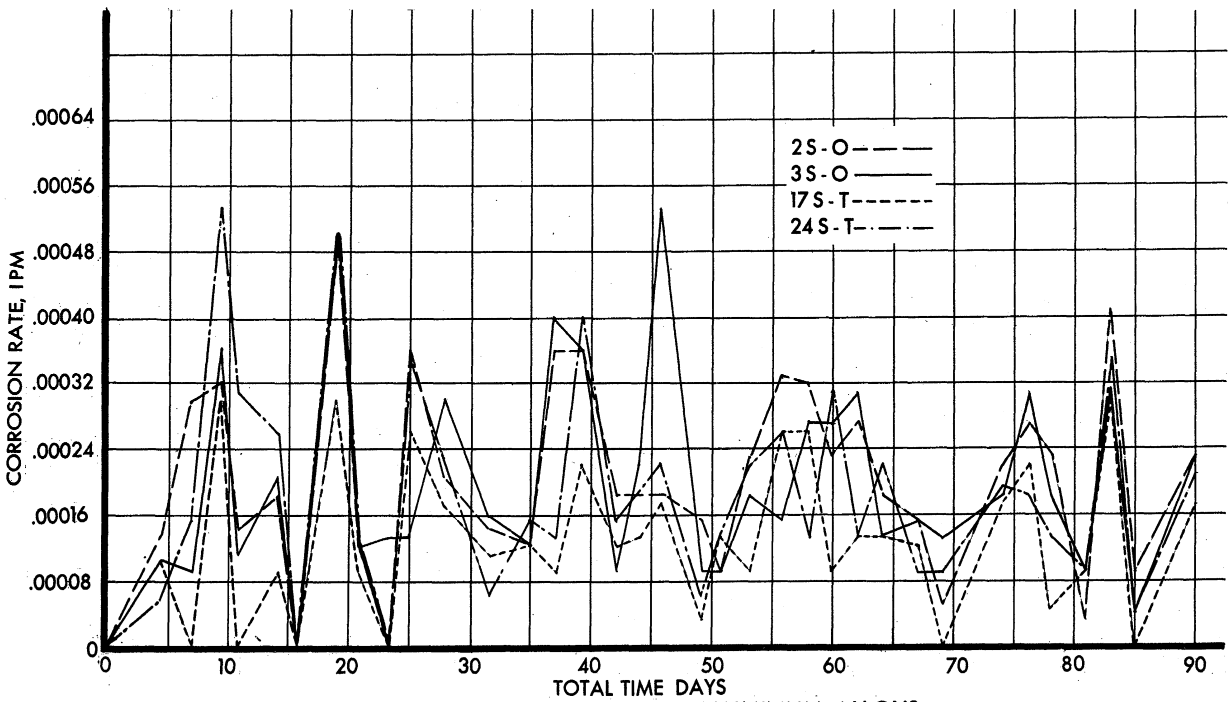

FIG. 6 SERIES II CORROSION OF ALUMINUM ALLOYS
Continuous exposure to both liquid and fumes of WFNA

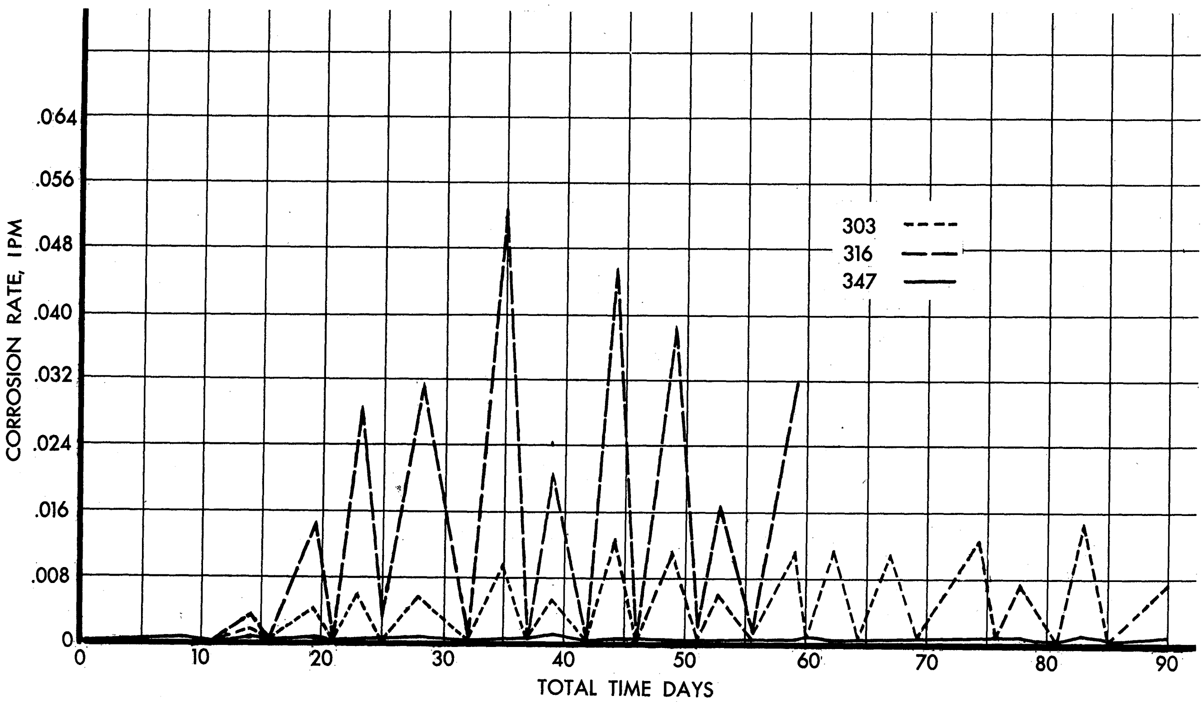

FIG. 7 SERIES III: CORROSION OF STAINLESS STEELS

Alternate Exposure to WFNA & Dilute HNO_3 (Higher rates in WFNA)

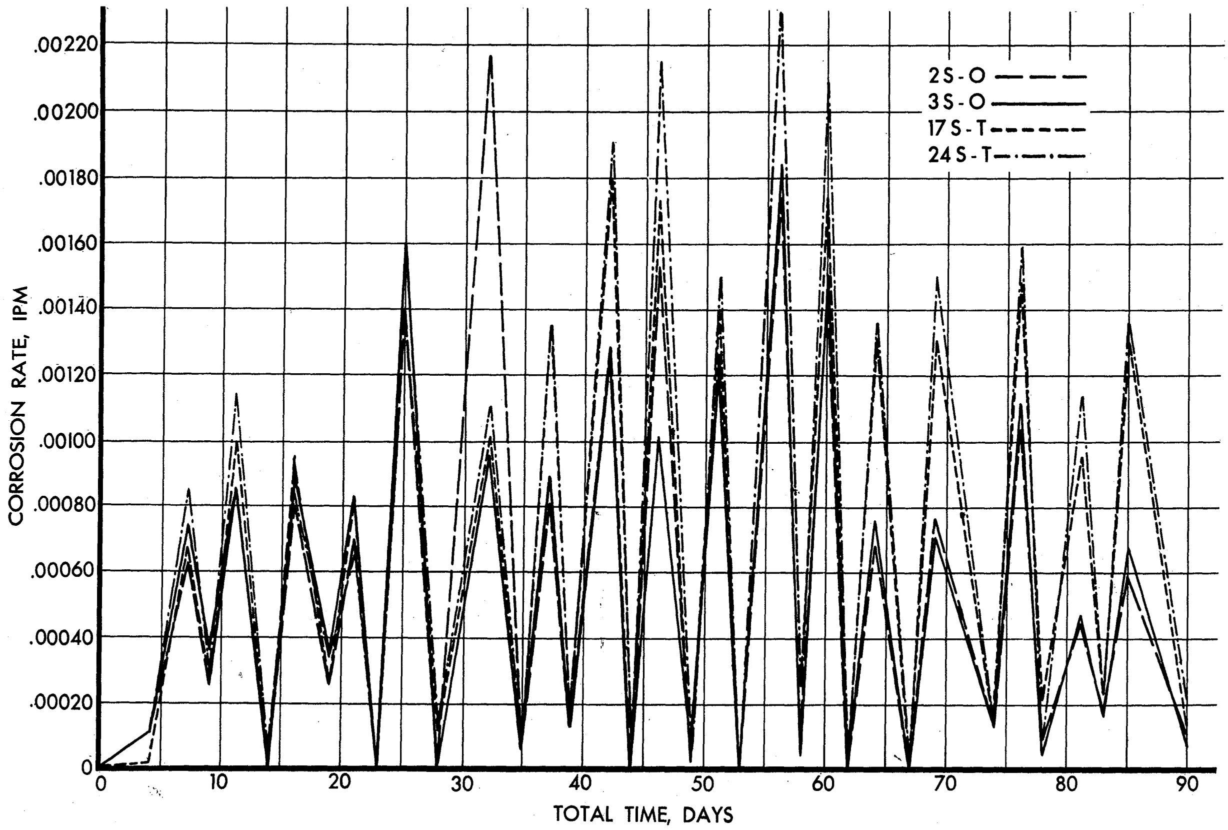

FIG. 8 SERIES III: CORROSION OF ALUMINUM ALLOYS

Alternate exposure to WFNA and dilute HNO_3 (Higher rates in dilute acid)

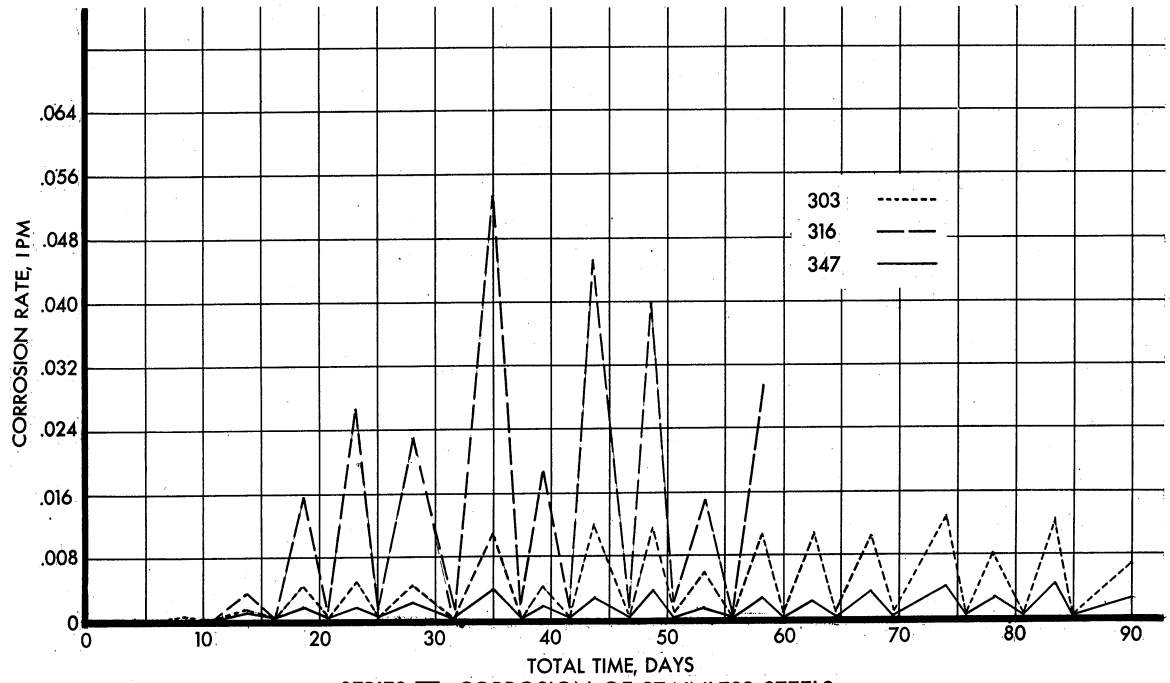

FIG. 9 SERIES IV: CORROSION OF STAINLESS STEELS

Alternate exposure toWFNA and to air after water rinse (Higher rates in WFNA)

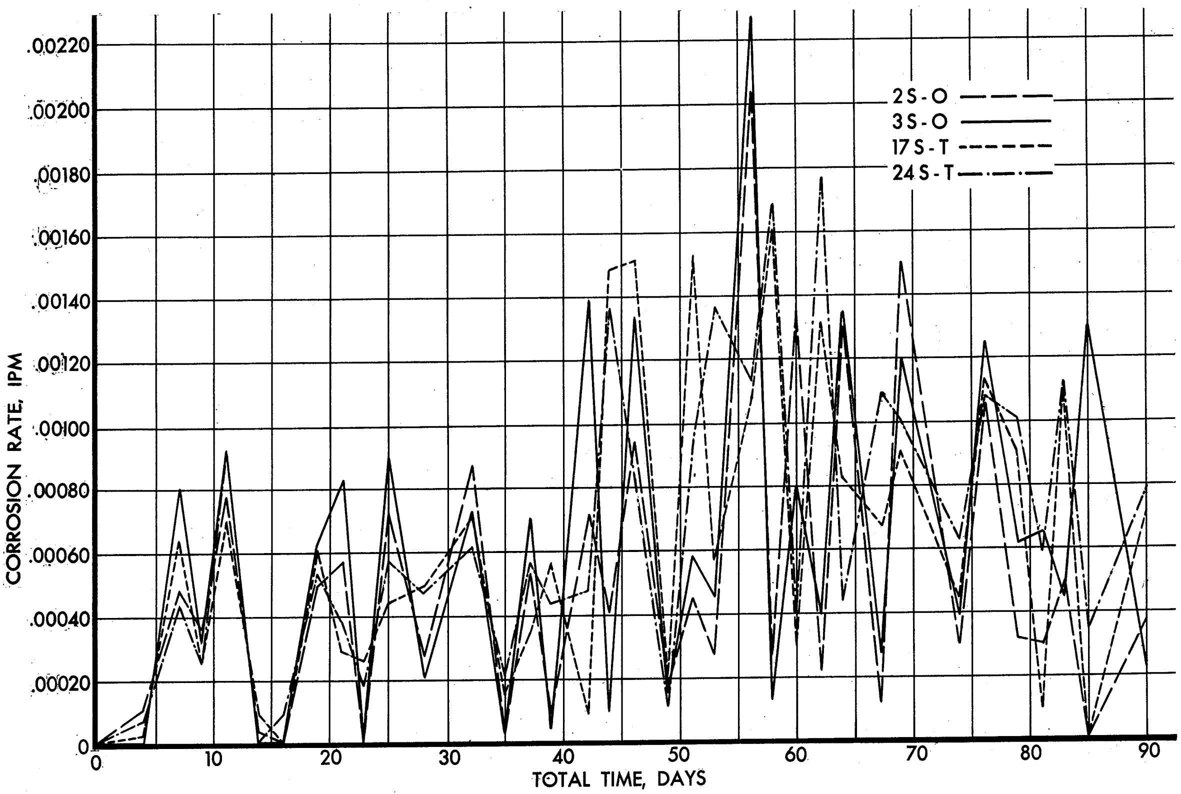

FIG. 10 SERIES IV: CORROSION OF ALUMINUM ALLOYS

Alternate exposure to WFNA and to air after water rinse (Higher rates in air)

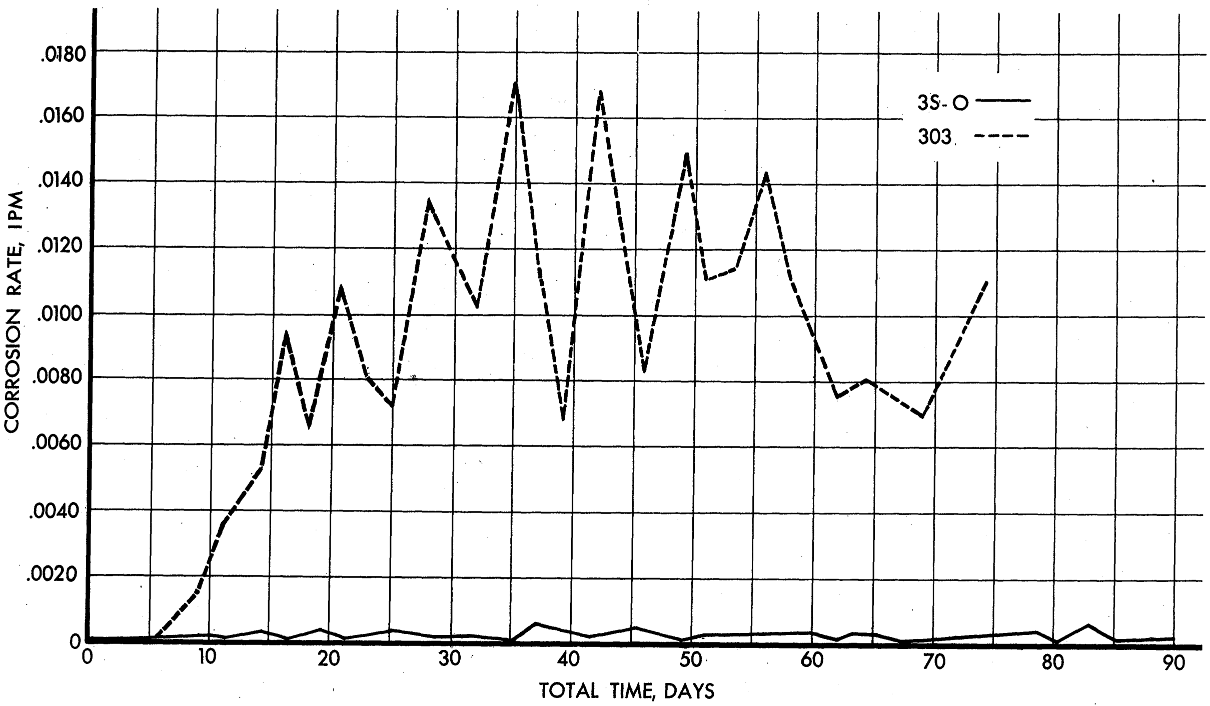

FIG. 11 COMPARISON OF REPRESENTATIVE STEEL & ALUMINUM ALLOY SAMPLES IN WFNA

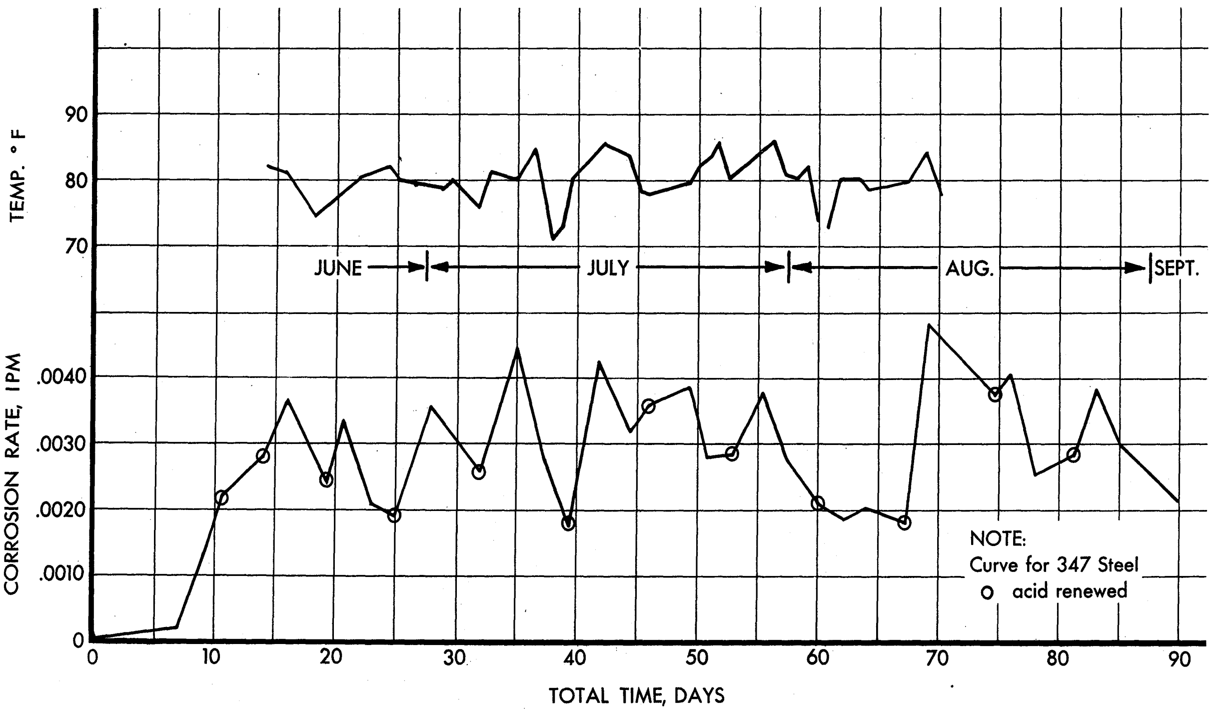

FIG. 12 FACTORS IN IRREGULARITY OF CORROSION RATES OF STEELS

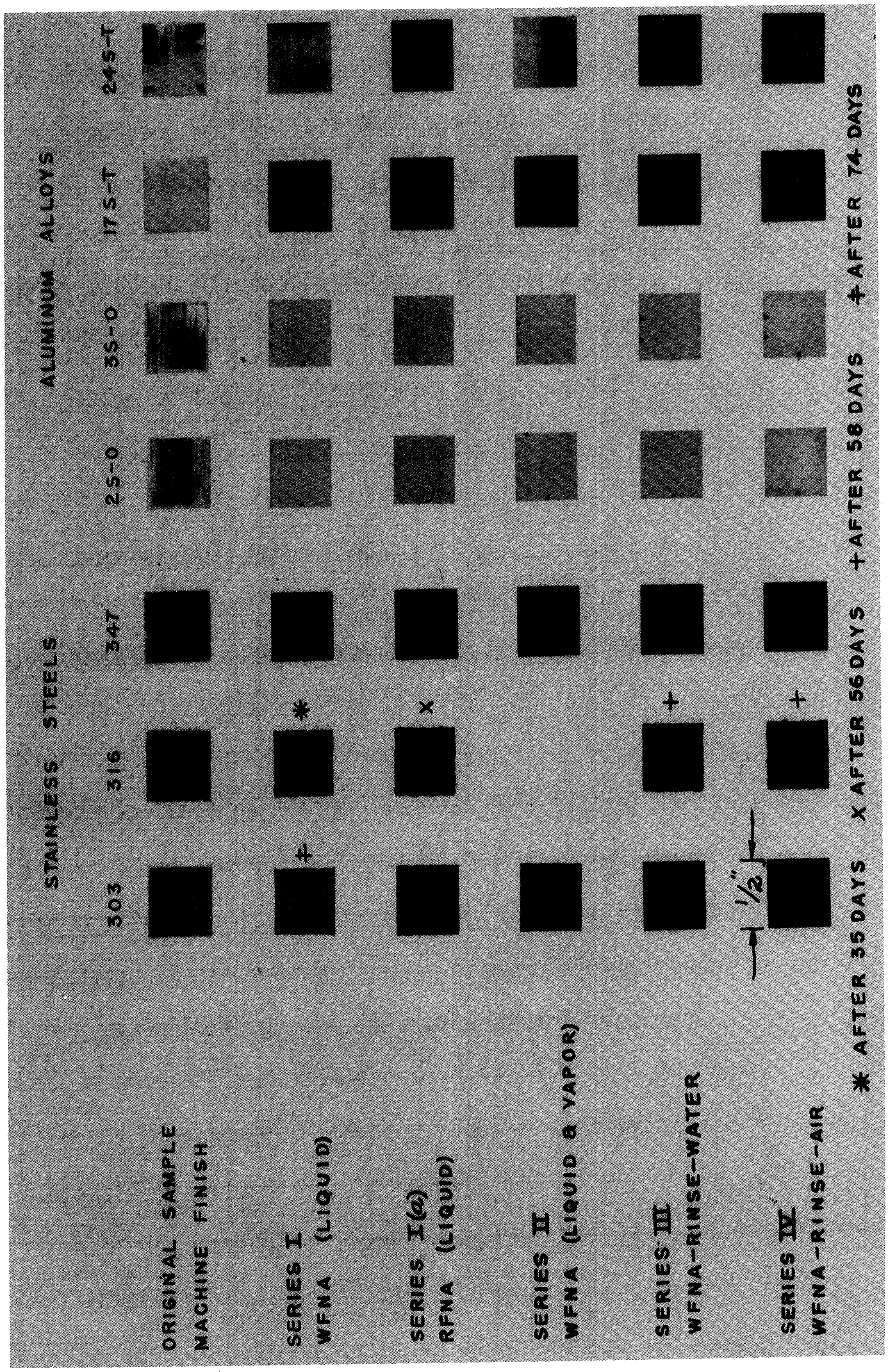

FIG. 13 STEEL AND ALUMINUM SAMPLES AFTER NINETY-DAY CORROSION TESTS

FIGURE 14: AVERAGE CORROSION RATES IN IPM OF STAINLESS STEEL AND ALUMINUM ALLOYS IN WFNA

WFNA: Comm. 98% Room Temperature Test Period: 90 days

		Stainless Steels			Aluminum Alloys			
Series		303	316	347	2S-0	3S-0	17S-T	24S-T
I	WFNA liquid	.00938**	.02460+	.00264	.00023	.00025	.00015	.00022
Ia	RFNA liquid	.00216*	.01290*	.00068*	.00032*	.00033*	.00020*	.00030*
II	WFNA liquid and vapor	.00506		.00192	.00018	.00019	.00012	.00018
III (seventeen) cycles)	WFNA (rinse) Water	.00742 .00092	.02180* .00060*	.00259 .00004	.00005 .00101	.00007 .00100	.00009 .00127	.00012 .00141
IV (seventeen cycles)	WFNA (rinse) Air	.00731 .00015	.02180* .00107*	.00245 .00005	.00022 .00084	.00020 .00099	.00057 .00060	.00066 .00063

*56-62 days

**74 days

+35 days

FIGURE 15: AVERAGE CORROSION RATES IN IPM OF STAINLESS STEEL AND ALUMINUM ALLOYS IN RFNA

RFNA: Comm. 6.5% Room Temperature Test Period: 90 days

Series		Stainless Steels 303	Stainless Steels 316	Stainless Steels 347	Aluminum Alloys 2S-0	Aluminum Alloys 3S-0	Aluminum Alloys 17S-T	Aluminum Alloys 24S-T
I	RFNA liq.	.00455	.01280*	.00156	.00026	.00027	.00015	.00026
II	RFNA liq. and vap.	.00113	.00461**	.00036	.00051	.00028	.00025	.00030
III (eleven cycles)	RFNA (rinse)	.00276	.00505**	.00106	.00009	.00015	.00013	.00015
	Water	.00002	.00043**	.00001	.00070	.00085	.00073	.00081
IV (eleven cycles)	RFNA (rinse)	.00395	.01490**	.00139	.00020	.00016	.00017	.00027
	Air	.00002	.00076**	.00001	.00060	.00077	.00073	.00058
V (eleven cycles)	RFNA	.00398	.01480	.00109	.00015	.00013	.00019	.00020
	Air	.00001	.00063	.00005	.00075	.00081	.00084	.00082

*After 50 days.
**After 75 days total.

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