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EVALUATION OF THE EFFECTS OF CONTAMINATION BY SILICATES OF ANODIZING SEAL WATER

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Summa Corporation

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July 1973

EVALUATION OF THE EFFECTS OF CONTAMINATION
BY SILICATE OF ANODIZING SEAL WATER

FINAL REPORT
Report HH 73-44

By

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1 ppm



Frontispiece. Effect of Silicates in Seal Water on Corrosion Resistance of Anodized Aluminum

FOREWORD

Previous tests conducted by Hughes Helicopters in 1968 indicated that there is a relationship between silicate contamination and corrosion of anodized aluminum. Based on this evidence AVSCOM awarded a contract for the purpose of conducting tests to verify this relationship.

Under this contract, Hughes Helicopters has conducted a series of laboratory tests on aluminum specimens in conjunction with the silicate level in the seal water following aluminum anodizing. The objectives were to determine the effects on the subsequent resistant to corrosion, when subjected to the standard salt spray test, and the effects on bond strength as measured by standard T-peel tests. This work was conducted in the Materials and Processes Laboratory, Hughes Helicopters, Culver City, California, in the period May to July 1973.

This work was accomplished under contract DAAJ01-73-C-0378(P3L) between Hughes Helicopters and AVSCOM.

SUMMARY

An evaluation of the effects of contamination by silicates in the seal water on chromic acid anodized aluminum was performed for AVSCOM. The basic objectives of this program were:

1. To establish an empirical correlation between the amounts of silicate present in boiling deionized sealing water and the subsequent resistance to corrosion of chromic acid anodized aluminum when subjected to the standard salt spray test.
2. To establish the effect of silicates in the rinse water following aluminum anodizing on the adhesive bond strength as measured by standard T-peel tests.

The results of this program indicate that the resistance to corrosion was drastically reduced as the silicates increased above 4 parts per million. The amount of corrosion obtained was in proportion to amounts of silicates from 3 to 10 parts per million.

No effect was found on adhesive bond strength when rinsing, following chromic acid anodizing, with water containing 1 to 100 parts per million of silicate.

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TECHNICAL DISCUSSION

SELECTION OF SILICATE TEST PROCEDURE

Reference 1 was used as the basis for test for silicate level. From this reference the molybdosilicate method was chosen. Standard solutions were prepared from chemically pure sodium metasilicate as recommended.

In attempting to prepare a calibration graph for use of the DU Spectrophotometer, it was found that the transmission percentages continued to drop with time, even though the Reference 1 instructions recommend that readings be taken between 2 and 15 minutes after adding oxalic acid. Further work indicated that if the oxalic acid was omitted, the readings stabilized. Table I and Graph I illustrate this. The purpose of the oxalic acid is to prevent interference by phosphates. This step was dropped from the procedure in preparing the calibration graph and in the subsequent testing.

Deionized water from a large production unit is piped to the Hughes Laboratory. This water was checked for silicates along with bottled water and redistilled water. All contained a minimum of 0.2 to 0.5 ppm (parts per million). Consequently the deionized water was used for the tests in this program. In establishing the calibration graph, additions based on calculations were made to the deionized water and the resulting percent transmission plotted against parts per million of silicate added. This curve did not pass through the 100 percent transmission point due to the silicates already present in the deionized water. Consequently, the calibration curve was offset to permit this, thus furnishing true silicate values. See Table II and Graph II.

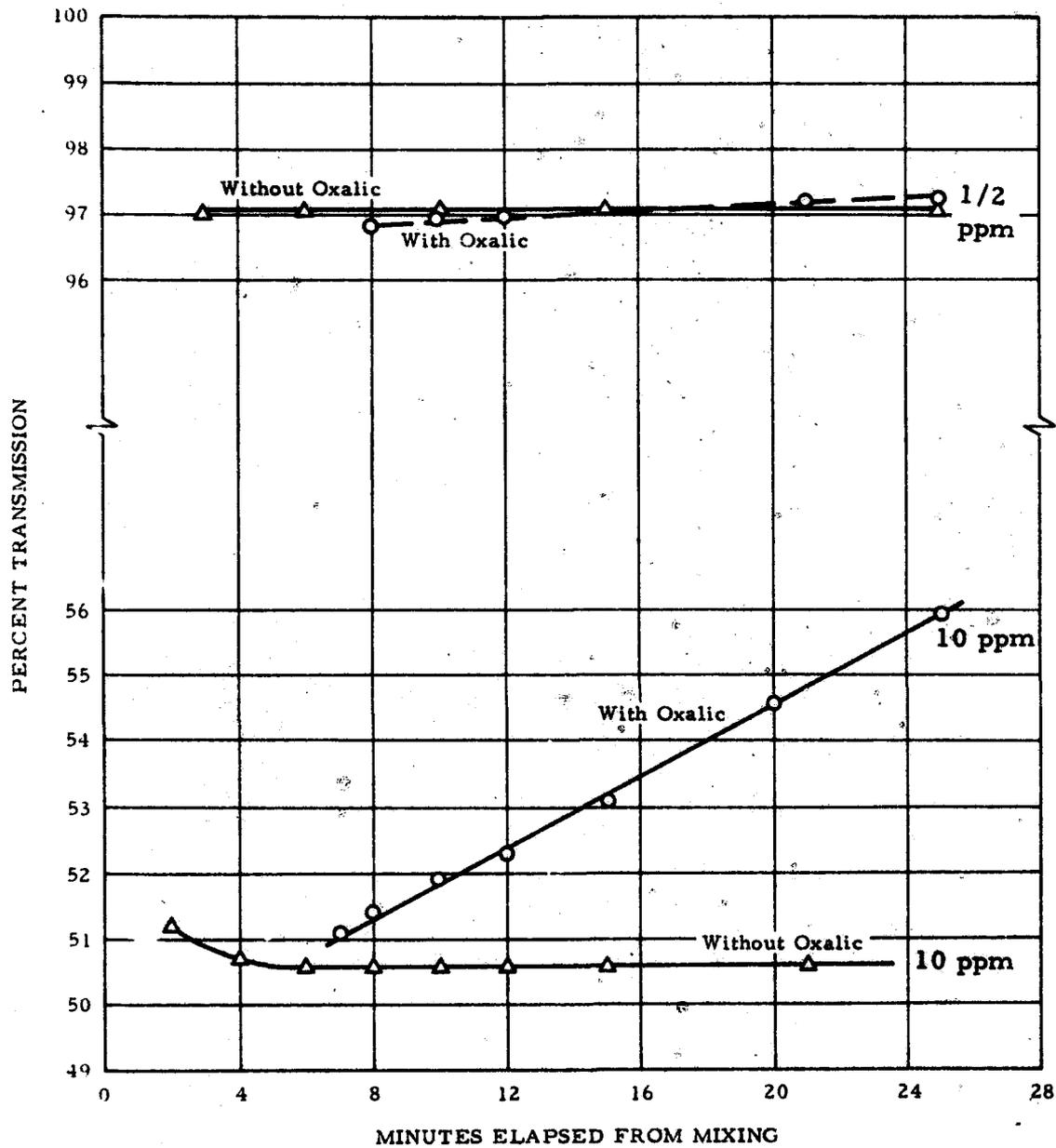
PRELIMINARY TESTING

Since no water was available with zero ppm silicates, as discussed above, this lot was dropped from the trials. Sealing solutions were prepared in 4-liter stainless steel beakers by adding the following amounts of 100 ppm stock silicate solution to the deionized water in the

Reference 1. Standard Methods for Examination of Water and Waste Water, American Public Health Association, Inc., 1965 Edition pp 258-264.

TABLE I. EFFECT OF TIME ON TRANSMISSION READINGS
OF SPECTROPHOTOMETER FOR SILICATES

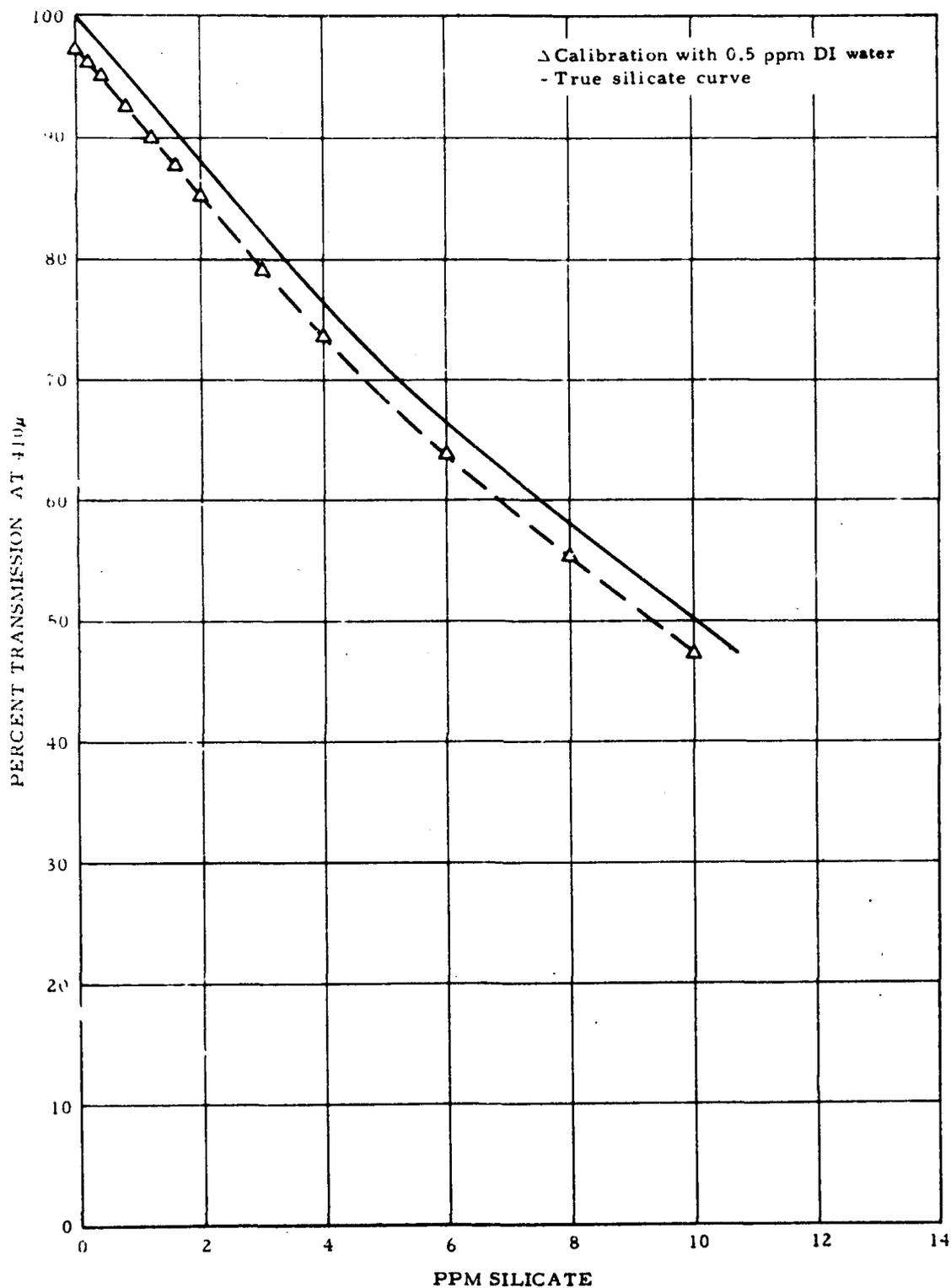
| Silicate | Without Oxalic Acid | | With Oxalic Acid | |
|----------|-------------------------|-------------------------|-------------------------|-------------------------|
| | Elapsed Time Minutes | Percent Transmission | Elapsed Time Minutes | Percent Transmission |
| 1/2 ppm | 3 | 97.0 | 8 | 96.8 |
| | 6 | 97.1 | 10 | 97.0 |
| | 10 | 97.1 | 12 | 97.0 |
| | 15 | 97.1 | 15 | 97.0 |
| | 25 | 97.1 | 21 | 97.2 |
| | | | 25 | 97.2 |
| 10 ppm | 2 | 51.2 | 7 | 51.1 |
| | 4 | 50.7 | 8 | 51.4 |
| | 6 | 50.6 | 10 | 51.9 |
| | 8 | 50.6 | 12 | 52.3 |
| | 10 | 50.6 | 15 | 53.1 |
| | 12 | 50.6 | 20 | 54.6 |
| | 15 | 50.6 | 25 | 55.9 |
| | 21 | 50.6 | | |



Graph I. Transmission Readings for Silicate on DU Spectrophotometer.

TABLE II. DU SPECTROMETER CALIBRATION FOR SILICATES

| 10 PPM Standard Mls | DI Water Mls | Silicates PPM Added | Percent Transmission |
|---------------------------|-----------------|------------------------|-------------------------|
| 0 | 50 | 0 | 97.2 |
| 1 | 49 | 0.2 | 96.1 |
| 2 | 48 | 0.4 | 94.8 |
| 4 | 46 | 0.8 | 92.5 |
| 5 | 45 | 1.0 | 91.0 |
| 6 | 44 | 1.2 | 89.9 |
| 8 | 42 | 1.6 | 87.6 |
| 10 | 40 | 2.0 | 85.0 |
| 15 | 35 | 3.0 | 79.0 |
| 20 | 30 | 4.0 | 73.6 |
| 30 | 20 | 6.0 | 63.9 |
| 40 | 10 | 8.0 | 55.5 |
| 50 | 0 | 10.0 | 47.6 |



Graph II. Spectrophotometer Calibration.

beakers: 1/4 ppm - none, 1 ppm - 3 mls; 3ppm - 11 mls; 5 ppm - 19 mls; 10 ppm - 39 mls. The pH of the deionized water had been adjusted to 5.7 prior to addition of the silicate solution.

The test panels for corrosion testing were 3 by 10 by 0.032 inches 2024T3 aluminum alloy per QQ-A-250/4. The test panels were anodized in the production unit under the following conditions. Temperature, 100° F; voltage, 40 volts; and time, 30 minutes. Five panels were then sealed in each of the 4-liter beakers at 205° F for 15 minutes. They were then placed in the salt spray unit. The anodize coating weight was 441 mg/square feet.

The next day the solutions, cooled to room temperature, were checked for silicate content and for pH with the following results:

| <u>Silicates (Calculated Based on Known Addition)</u> | <u>Percent Transmission Measured</u> | <u>PPM (From Calibration Graph)</u> | <u>pH Measured</u> |
|---|--|---|------------------------|
| 1/4 | 96.8 | 0.5 | 6.60 |
| 1 | 94.6 | 0.9 | 7.65 |
| 3 | 93.5 | 1.1 | 7.85 |
| 5 | 86.5 | 2.2 | 8.05 |
| 10 | 79.1 | 3.5 | 8.25 |

The reduced silicate content of the sealing solutions indicated that much of the silicate was absorbed by the panels, thus lowering the solution concentration. (This might have been due to the relative small size of the liquid container.) Also, the pH of the stock silicate solution was found to be 11.95. It was evident that the minute amounts of silicate added to the sealing solution had raised the pH of the sealing solutions above the control range. As result of these variations from the intended test levels, the salt spray panels tested in these solutions did not show the expected differences in corrosion level.

In order to prevent recurrence of the above, a 15-gallon stainless steel tank was bought for the balance of the test program. In using this 15-gallon tank, arrangements were made to withdraw a sample of the hot sealing solution, cool and test it, and then adjust both the pH and silicate content to the proper test levels immediately before sealing each

successive lot. To reduce the amount of pH adjustment, the stock solution of silicate was adjusted to a pH of 5.7 prior to introduction into the test solutions.

On the next trial excessive amounts of stock silicate solution were necessary to obtain the required silicate content in the test solution. The content of the stock silicate was rechecked and found to be low. In two days it had dropped from 1000 ppm to 150 ppm. A fresh solution was made up (4.73 gm/liter) and acidified to 5.7 pH. It dropped to 650 ppm in two hours. A stock solution a week old which had not been acidified still remained at 1000 ppm. It would appear that the stock solution is stable at high pH but not at an acid pH. In the "Discussion of Interferences" in the Reference 1 instructions, a form of silicate was mentioned which does not give the molybdosilicate reaction. It would seem that low pH is conducive to conversion of the silicate to this form.

In the final tests the silicate stock solution was added in the alkaline form. The pH was then adjusted in the test solution tank.

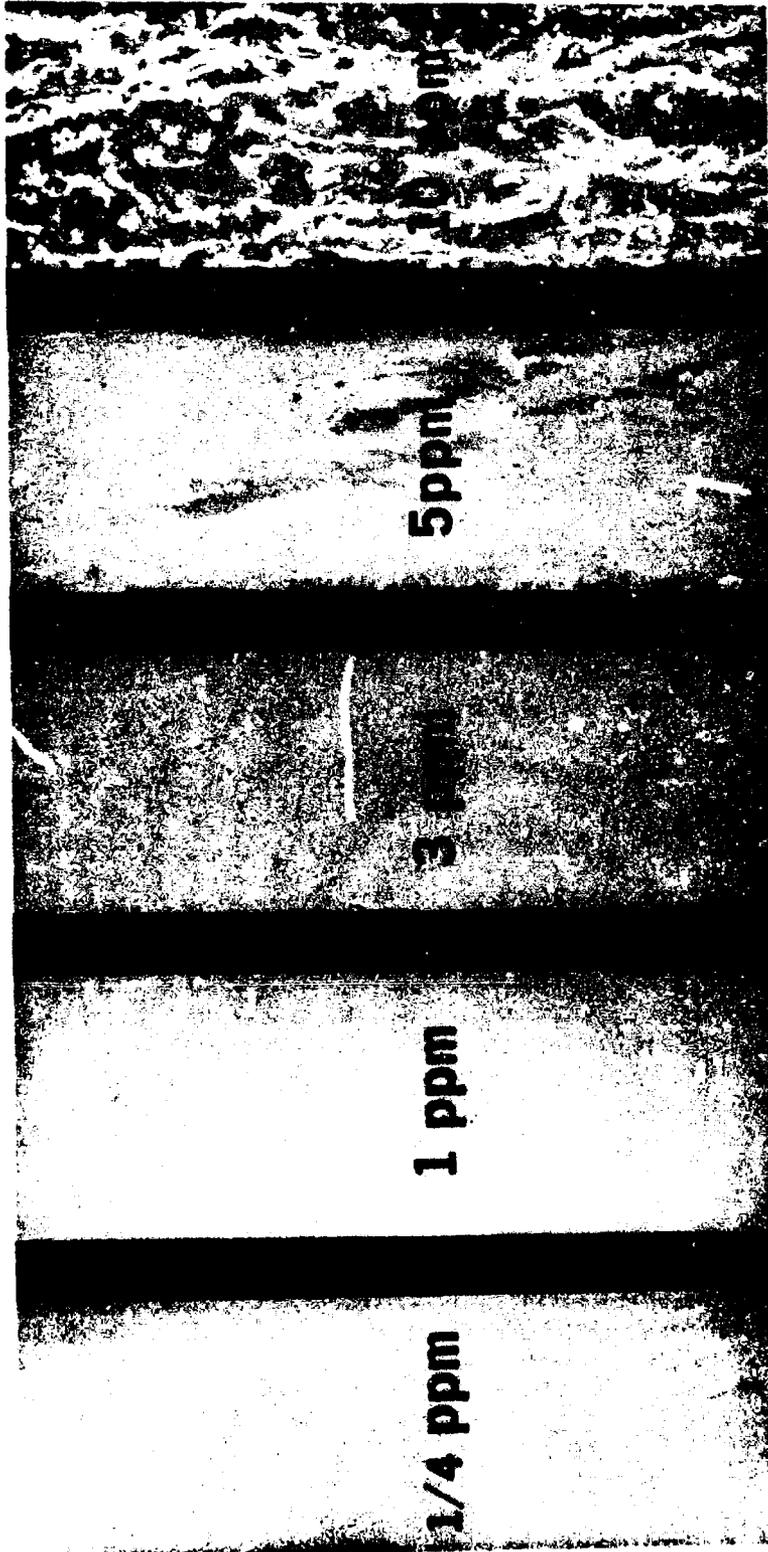
SEALING AND SALT SPRAY TESTING PROCEDURE

Additional test panels were anodized in the production unit at 98° F and 39 volts for 30 minutes. This gave a coating weight of 345 mg/square foot. Reference 2 specifies a minimum of 200 mg/square foot. Three sets of these were sealed successively in the 15-gallon tank in boiling deionized water at 5.7 to 4.8 pH for 15 minutes. (Reference 2 specifies boiling deionized water.) Final silicate concentration determined immediately preceding sealing were as follows: 0.4, 1.3, 3.0, 5.8, and 9.8. These panels were given 336 hours in the salt spray unit. They gave definite evidence of a correlation between increasing amounts of silicates and worsening corrosion. These panels are illustrated in Photo No. 1 of this report. A definite difference in the corrosion level is exhibited between 3 and 5 ppm of silicate and a much greater difference between 5 and 10 ppm.

Two sets of additional panels ranging from 1 to 10 parts per million of silicate were prepared. The silicate in the seal water was added, as

Reference

1. Standard Methods for Examination of Water and Waste Water, American Public Health Association, Inc. 1965 Edition pp 258-264.
2. MIL-A-8625, Anodic Coating, For Aluminum and Aluminum Alloys



CORROSION SPECIMENS

Photo 1

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calculated, without acidification, and the pH adjusted just before sealing. The silicate content was also checked with the spectrophotometer. These panels were sealed for 15 minutes at a pH of 5.5 to 5.9 and a temperature of 211 to 212° F. Photo No. 2 illustrates these panels. They confirm the previous results.

RINSING, BONDING, AND T-PEEL

Panels used for bonding were 4 by 7 by 0.025 inches, 2024T3 aluminum alloy, both Alclad (QQ-A-250/5) and bare (QQ-A-250/4). Four sets of panels were anodized in the production unit at 98° F and 39 volts for 30 minutes. These were then brought to the laboratory and rinsed successively in the 15-gallon tank at 95° F and a pH of 5.4 for 10 minutes. (Reference 3 specifies 90 to 100° F at 5.2 to 5.8 pH for 3 minutes.)

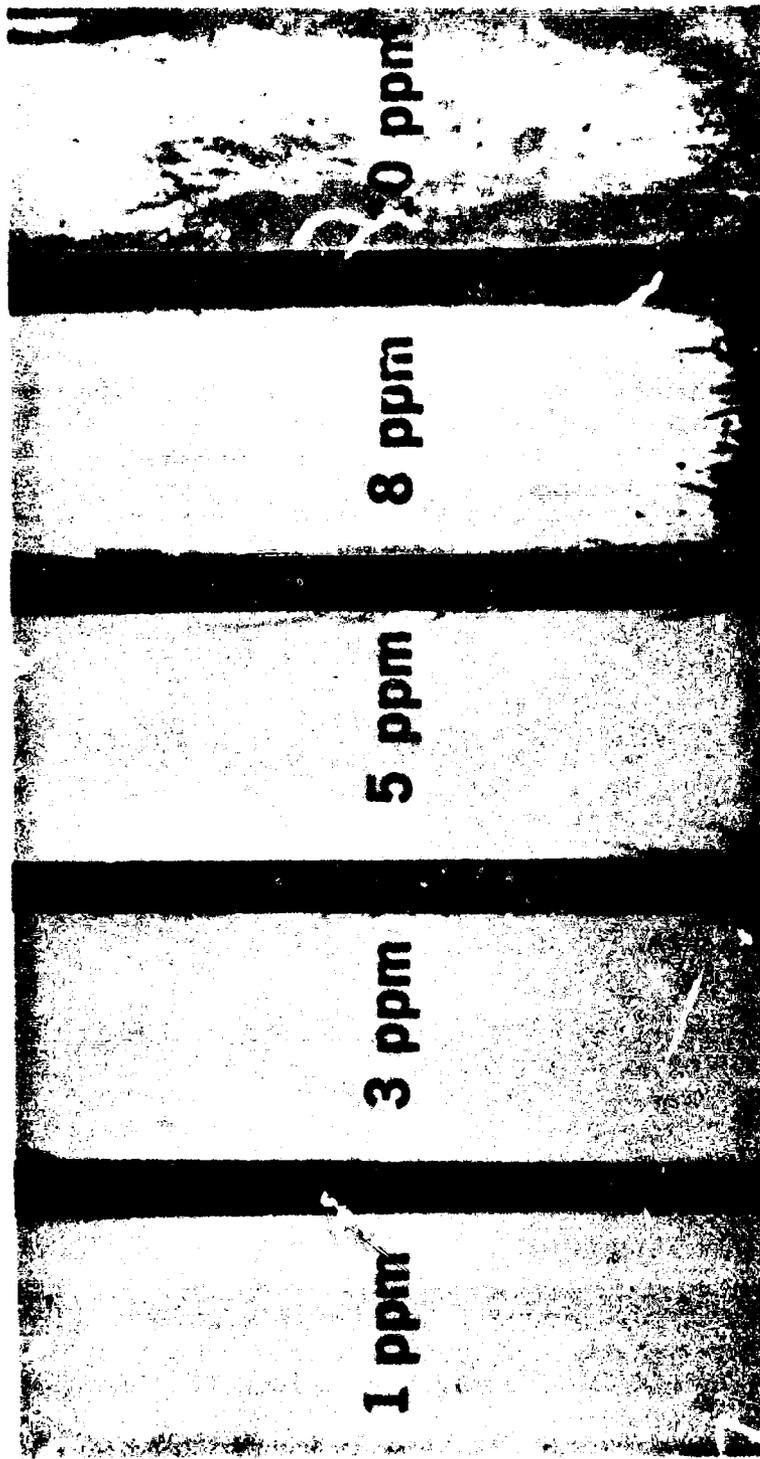
Note: Panels used for bonding are not sealed. The coating weight for the Alclad panels was 655 mg/square foot and for the bare panels 442 mg/square foot. The results of silicate verification just before rinsing were: 0.4, 1.3, 3.6, 6.1, and 11.0 respectively. These panels were then primed with EA9210 primer and cured. They were next bonded in pairs with FM-123 film adhesive in a platen press for 60 minutes at 250° F and 70 psi (Reference 4 and 5).

After cutting 1/2-inch scrap from each edge of the 4-inch bonded panels, they were sheared into three 1-inch test strips. The unbonded 1-inch at one end of each strip was then pried open and inserted in the clamps of a Tinius Olsen tensile machine. This T-peel test was pulled at 10 inches per minute. The pounds of pull were recorded on a roll chart. Graph III gives typical results of these charts. The data obtained from these panels is tabulated in Table III. This data is also plotted on Graph IV.

An additional six sets of 4 by 7 by 0.25 inches (three bare and three Alclad) panels were anodized in production at 100° F and 40 volts for 30 minutes. The coating weight of the Alclad panels was 536 mg/square foot and of the bare panels 310 mg/square foot. These were also primed, bonded,

Reference

3. Hughes Process Specification, HP 4-35, Anodic Treatment of Aluminum Alloys for Metal-to-Metal Bonding.
4. EA9210, Adhesive Primer, manufactured by Hysol Division of Dexter Corporation.
5. FM123, Film Adhesive, manufactured by American Cynamide Company.

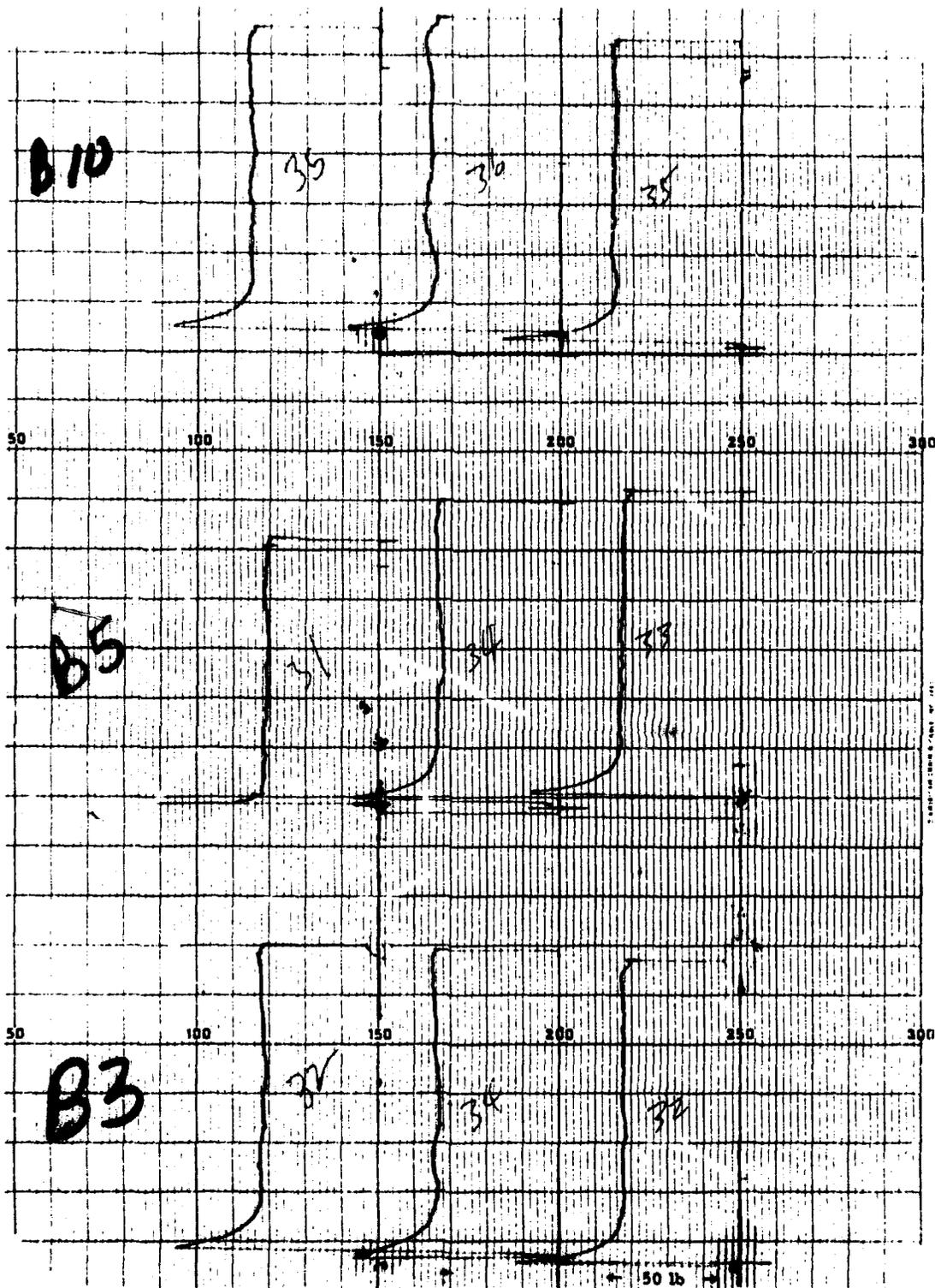


CORROSION SPECIMENS

Photo 2

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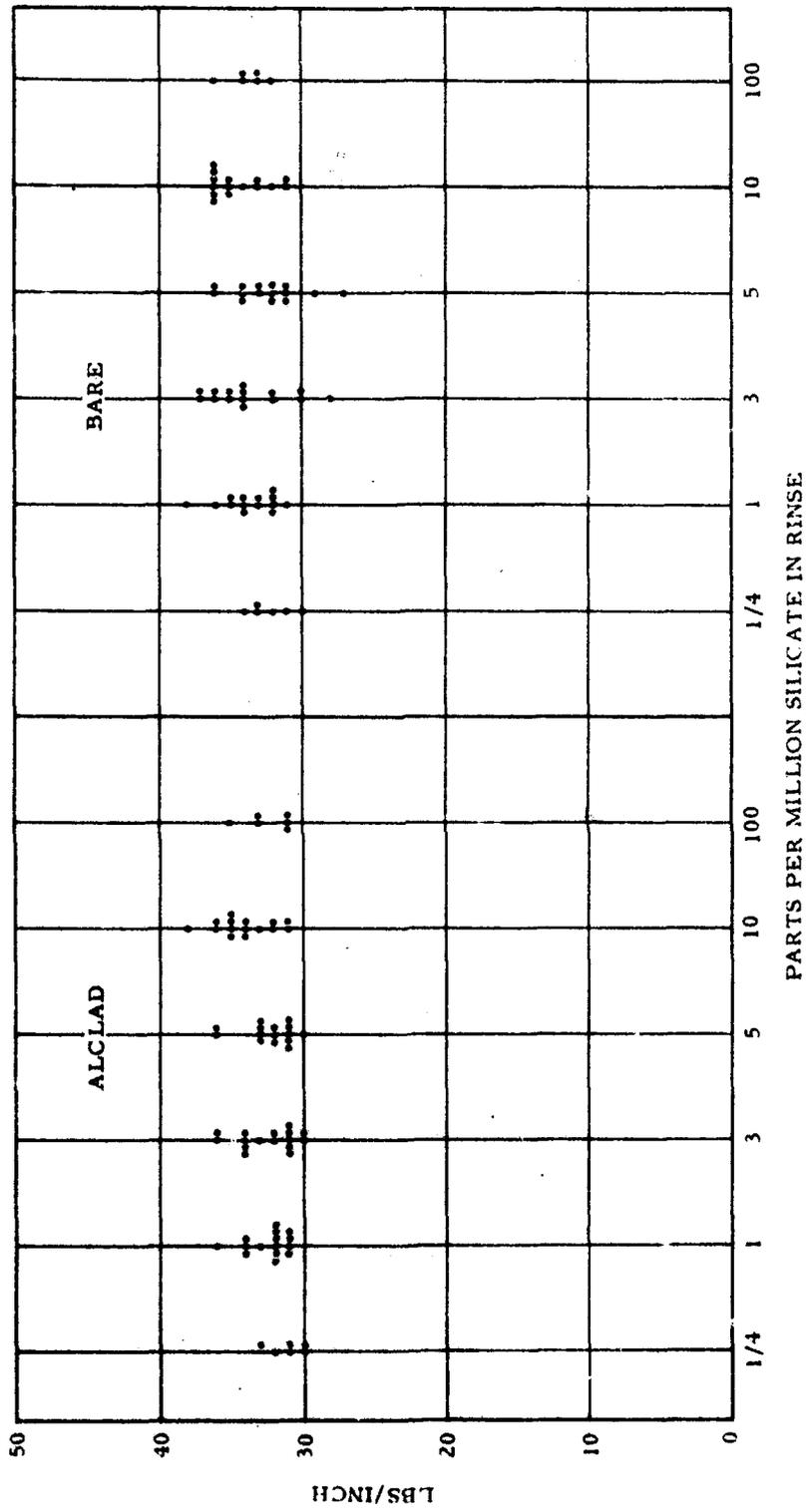


Graph III. T-Peel, Pull at 10 Inches Per Minute

TABLE III. T-PEEL TESTS ON BONDED SAMPLES

| PPM | 6/6/73 | | | 6/20/73 | | | Average |
|-------|----------|----------|----------|----------|----------|-----|---------|
| A 1/4 | 31-32-30 | 30-31-33 | --- | --- | --- | --- | 31.17 |
| A1 | 32-33-31 | 32-31-32 | 31-31-32 | 32-34-32 | 34-36-34 | --- | 32.47 |
| A3 | 31-33-31 | 30-31-32 | 30-31-32 | 34-36-34 | 34-36-34 | --- | 32.60 |
| A5 | 31-32-30 | 31-33-32 | 31-32-36 | 31-33-31 | 33-36-33 | --- | 32.33 |
| A10 | 34-36-34 | 32-34-33 | 35-35-38 | 31-32-31 | 35-36-35 | --- | 34.07 |
| A100 | --- | --- | 33-35-31 | 31-33-31 | --- | --- | 32.33 |
| B 1/4 | 33-34-33 | 31-30-32 | --- | --- | --- | --- | 32.17 |
| B1 | 33-34-32 | 29-31-32 | 33-34-38 | 32-35-32 | 34-36-35 | --- | 33.33 |
| B3 | 32-34-32 | 28-30-30 | 34-34-36 | 35-37-37 | 34-36-35 | --- | 33.60 |
| B5 | 31-34-33 | 31-27-29 | 32-32-36 | 31-33-32 | 34-36-34 | --- | 32.33 |
| B10 | 35-36-35 | 35-33-31 | 33-36-36 | 31-34-32 | 36-36-36 | --- | 34.33 |
| B100 | --- | --- | 33-34-36 | 33-34-32 | --- | --- | 33.67 |

A Samples are Alclad 2024 aluminum
 B Samples are Bare 2024 aluminum

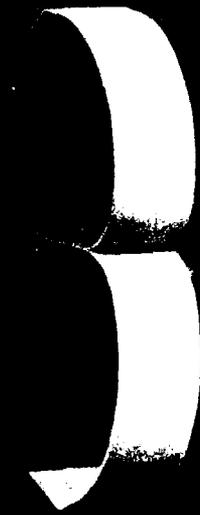


Graph IV. T-Peel Test Results on Bonded Panels.

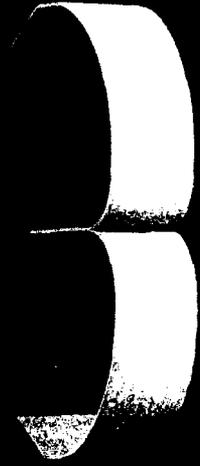
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T-PEEL SPECIMENS adhesively bonded

Bare 2024-T3



1/4 ppm



10 ppm



100 ppm



Alclad 2024-T3

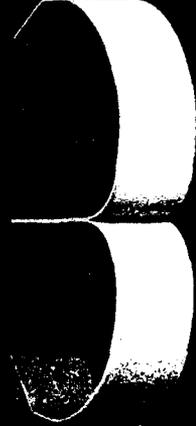


Photo 3

sheared and pulled on the Tinius Olsen. Results from these are also tabulated in Table III and plotted in Graph IV.

Photo No. 3 is typical of all the specimens pulled and shows 100 percent cohesive failure.

The adhesive bond strength was not affected by silicates in the rinse water after anodizing.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. The resistance to corrosion was drastically reduced when the silicate content of the seal water was increased from 1 to 10 parts per million with a pronounced difference in corrosion level between 3 and 5 parts per million.

Note: These tests were run at a pH of 5.5. to 6.0.

2. No effect was found on bond strength with deionized water containing from 1 to 100 parts per million as the final rinse.

Note: These panels were not sealed.

RECOMMENDATION

1. It is recommended that an addition be made to paragraph 3.11.1 of MIL-A-8625C stating: "Deionized sealing water shall contain a maximum of 4 parts per million of silicate."

Note: The above recommended control has been incorporated into Hughes Helicopters specifications and will be used in processing parts for the military helicopters, including the Advanced Attack Helicopter.

REFERENCES

1. Standard Methods for Examination of Water and Waste Water, American Public Health Association, Inc. 1965 Edition pp 258-264.
2. MIL-A8625, Anodic Coating, For Aluminum and Aluminum Alloys.
3. Hughes Process Specification, HP 4-35, Anodic Treatment of Aluminum Alloys for Metal-to-Metal Bonding.
4. EA9210, Adhesive Primer, manufactured by Hysol Division of Dexter Corporation.
5. FM123, Film Adhesive, manufactured by American Cynamide Company.