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# ACCELERATED LABORATORY CORROSION TEST FOR MATERIALS AND FINISHES USED IN NAVAL AIRCRAFT

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## INTRODUCTION

In the middle 1960's the Aeronautical Materials Laboratory recognized the fact that salt spray tests in a 5% or 20% MaCl environment were not accurately predicting the behavior of materials and finishes used on naval aircraft. In service, high strength aluminum alloys such as 7075-T6 and 7178-T6 were experiencing exfoliation corrosion, not simply pitting. Paint systems were spalling from fastener patterns and highly stressed areas.

Studies indicated that the environment of an aircraft carrier included stack gas exhaust products is addition to sea spray. One of these products was sulfur dioxide. The presence or  $SO_4^{m}$  and the low pH (2.4-4.0) in moisture that accumulated on surfaces of aircraft parked on the flight deck of four different carriers was verified by an aircraft company (reference (a)).

Experiments were undertaken to create an accelerated laboratory testing environment that would more closely simulate that of an aircraft carrier.

Two approaches were examined; (1) introduction of  $SO_2$  directly into the salt spray cabinet at periodic intervals while the salt solution was continuously being sprayed, and (2) addition of  $SO_2$ ,  $H_2SO_3$  or  $H_2SO_4$  to the salt solution itself. At that time severe exfoliation corrosion was occurring on the 7178-T6 skins of a fighter aircraft so that allow and temper were used to select the optimum combination of conditions. It was found that introduction of  $SO_2$  into the chamber produced exfoliation corrosion that more closely resembled that occurring in service than did external additions to the salt solution. Conditions that produced exfoliation on 7178-T6 sheet in two weeks and that corresponded to the type produced during one to two years service life were arbitrarily chosen as those upon which to standardize.

In the ensuing years, modifications and refinements were made to the equipment and operating conditions, and a wide variety of materials used in naval aircraft were evaluated in this NaCl -  $SO_2$  environment. The materials included various aluminum alloys and heat treatments, electro-deposited coatings, fastener coatings, paints, sealants and preservative compounds.

Use of an  $SO_2$  laden salt fog is now being required for evaluation of materials and finishes for new generation aircraft and missiles. It is therefore necessary to promulgate a standardized procedure for salt -  $SO_2$  testing. The work required to do this was performed under reference (b). This report describes the test as it is now conducted at the Naval Air Development Center.



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#### EXPERIMENTAL PROCEDURE

Equipment and materials required for conducting a salt - SO<sub>2</sub> test are as follows:

1. Salt fog cabinet meeting requirements of ASTM B117-73, Appendix I.

2. Cylinder of SO<sub>2</sub> gas.

3. Flowmeter capable of measuring SO<sub>2</sub> gas flow of 1 cm<sup>3</sup>/min/ft<sup>3</sup> of cabinet volume (35 cm<sup>3</sup>/min/m<sup>3</sup>); also constructed of materials inert to  $SO_2$  gas.

4. Timer.

5. Two-way solenoid value fabricated of materials inert to SO2 gas.

6. Tubing and fittings for SO<sub>2</sub> line of materials inert to SO<sub>2</sub> gas.

The test consists of spraying salt fog continuously with introduction of  $SO_2$  gas directly into the chamber (not into the salt solution) for one hour four times a day, i.e., 1 hour/six hour cycle. A schematic of the  $SO_2$  line is shown in Figure 1.

It is highly desirable to have the SO<sub>2</sub> gas introduced into the chamber in such a way that a uniform dispersion throughout the interior will result. The UNIFOG dispersion tower can readily be adapted to provide for this as shown in Figure 2. Holes are drilled in the Plexiglas baffle at the top of the tower so that the gas comes out of eight uniformly spaced ports. The tower is located in the center of an eighteen or a thirty cubic foot box. For larger boxes, twin towers should be used.

There are undoubtedly other means for accomplishing a uniform dispersion of the gas. Introduction of the gas into the chamber through one or two tubes at the side should be avoided however.

Operating conditions for the test are as follows:

Bubble Tower Temperature - 46°C (115°F) Cabinet Temperature - 35°C (95°F)

SO<sub>2</sub> gas injection - 1 hr/6hr cycle SO<sub>2</sub> gas flow -1.0  $\pm$  0.2 cm<sup>3</sup>/min/ft<sup>3</sup> of box

\* Patanted, G. S. Equipment Division Harshaw Chemical Corporation 15533 Brookpark Road Glaveland, Ohio 44135

### CONDITIONS IN COLLECTION BOTTLE

#### (Tested Weekly)

1. 1 - 2 mls/br collection rate 2. pH - 2.5 - 3.2

All other aspects of the test should be conducted according to ASTM B117-73.

If synthetic sea salt is used instead of sodium chloride, the solution should be made in accordance with ASTM D1141-75, Standard Specification for Substitute Ocean Water, Section 6 (reference (c)).

#### DISCUSSION

When the NaCl - SO<sub>2</sub> test was first developed, Navy ships were using Navy Special Fuel Oil (NSFO) which had a maximum allowable sulfur content of 3%. The great majority have converted to using diesel fuel #2 which has a maximum allowable sulfur content of 1%, and all ships will be using this in the very near future. Actual sulfur content apparently varies according to the source of the fuel - some having 0.3 - 0.4% S, some having 0.7 - 0.8% S.

Discussions have been held with the Naval Ship Engineering Center, (MAVSEC) on more quantitatively characterizing the carrier environment (reference (d)). It is possible, knowing the sulfur content of the fuel, the amount consumed, and the percentage of excess air in which it is burned, to calculate the ppm of  $SO_2$  that will be discharged at the stack -"Static discharge" as it is termed. The level of operation of the boilers controls fuel consumption and this will vary with time. Maximum effluent is generated when planes are warming up for taka-off as the level of boiler operation is highest at that time.

Assuming a fuel with a sulfur content of 0.7 - 0.8%, being burned in 100% excess air, a volume concentration of 330 parts per million can be present at static discharge. With a sulfur content of 0.3 - 0.4% burned in 100% excess air, the volume concentration would be half of that value.

The amount of  $SO_2$  that will reach the planes parked on the flight deck depends on air currents, ship speed and weather conditions. These can wary from hour to hour. Obviously, this amount will be considerably less than that at static discharge.

In an effort to determine the relationship between the amount of  $SO_2$ at static discharge and that in the laboratory simulated carrier environment, calculations were made to convert the 25 cm<sup>3</sup>/min of  $SO_2$  being introduced into a 30 ft<sup>3</sup> cabinet into parts per million using the method

outlined in reference (a). A sample calculation is given below:

Density of SO<sub>2</sub> at 21°C (70°F) = 2.265 g/1 Considering 100Z R.H. at 750mm pressure and 35°C (95°F) Density correction for H<sub>2</sub>O vapor pressure at  $35^{\circ}C = 42.2mm$ 

> D moist air Dt dry  $\times \frac{P-0.3783e}{760}$ = 9.719  $\times \frac{750-(0.3783 \times 42.2)}{760}$ = 9.41  $\times 10^{-4}$ g/ml = 0.941 g/1

Considering chamber volume = 850 liters

SO<sub>2</sub> flow rate of 25 ml/min = 0.025 l/min

 $\frac{\text{SO}_2 \text{ content}}{\text{850 x density of SO}_2} = \frac{0.025 \text{ x density of SO}_2}{850 \text{ x density of moist air}}$ 

 $= 0.025 \times 2.265 = 70.75 \times 10^{-6} g$ 850 x 0.941

Approximation = 70 ppm

If the above assumptions are valid and reasonable, then during the one hour SO<sub>2</sub> portion of the cycle, approximately 70 ppm/minute of SO<sub>2</sub> is flowing into the chamber. This is less than that calculated for fuels with either 0.3 - 0.4% sulfur or 0.7 - 0.8% (115/330 ppm) at static discharge. Lacking more quantitative information, it is therefore believed that the currently used flow rate of 1.0  $\pm$  0.2 cm<sup>3</sup>/min/ft<sup>3</sup> of box is not unrealistic.

A cabinet in which 5% synthetic sea salt is used in place of 5% NaCl was put into operation several years ago. Limited correlative studics between the two cabinets have indicated that the synthetic sea salt/SO2 was less severe for unpainted aluminum alloys and more severe for cadmium plated steel than the MaCl/SO2 (Table I). Aluminum alloys protected by MIL-P-23377 primer and MIL-C-81773 topcoat showed no differences. The majority of environmental tests conducted to date at this Center, however, on metals, alloys, coatings and finishes, have been in the MaCl - SO2 fog.

A question frequently asked concerns the relationship between life of a finish or material in the selt fog test and its life in service on an aircraft. At this time such information does not exist. The comparison may in fact never be correlatable for organic materials, since sumlight (UV) plays a vital role in organic coating deterioration. It is planned to expose aluminum alloy specimens with various heat treatments on an aircraft carrier in the near future so that a time relationship can be determined.

#### CONCLUSIONS

The salt - 50<sub>2</sub> fog test has proved to be a valuable accelerated laboratory test for screening materials that have to survive service on neval vessels such as aircraft cerriers.

#### RECOMMENDATIONS

It is recommended that all materials and finishes to be used on new generation aircraft and missile/ be acreamed using the test method described in this report.

#### ACKNOWLEDGEMENTS

The contributions of Dr. V. Agarwala, Dr. D. Berman, Mr. S. R. Brown, and Mr. P. Sabatini to the test method described in this report are gratefully acknowledged.

#### REFERENCES

- (a) Private communication, Douglas Aircraft Company, Lorg Beach, California 1967.
- (b) AIRTASK A510-510C/001-4/7500-000-002 Work Unit A5203-88, "Material Deterioration Acalysis and Control" 1 October 1976.
- (c) ASTM D1141-75, Standard Specification for Substitute Ocean Water, Section 6.
- (d) Private communication from J. Boyle and M. Gorin, MAVSEC Philadelphia, 8 August 1977.

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(e) J. A. Dean (Ed.) Lange's Handbook of Chemistry, Elsventh Edition, p. 10-146, McGraw-Hill, 1973.

# TABLE I

COMPARISON OF CORROSIVITY OF 5% NeC1/SO2 AND 5% SYNTHETIC SEA SALT (SSS)/SO2

(SO<sub>2</sub> Flow Rate - 1.0  $\pm$  0.2 cm<sup>3</sup>/min/ft<sup>3</sup> of box)

<u>Material</u>	One Week		Two Weaks	
	<u>855</u>	NeC1	<u>838</u>	HaC1
Chromated 2024-T3	Numerous Pits		48 pite/in	<sup>2</sup> 80 pits/in <sup>2</sup>
Cd plated 1010 Steel & Chromate	65-75% rust	25-45% rust	100% rust (heavy)	100% rust (moderate)
7178-T6 Aircraft Skin	Slight Corrosion		Pitting only	y Exfoliation
7075-T6/Graphite Epoxy Fatigue Specimens	Slight Atta	ack on 7075	<pre>* 15,700/9900 cycles to failure</pre>	* 8000/9000 cycles to failure

Note: Two panels of each of the above materials were exposed.

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\* Fatigue tested at ambient conditions at 233 cycles/min.





FIGURE 2 - Interior View of Salt - SO<sub>2</sub> Fog Cabinet

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