

Atmospheric and Surface Effects and the Fatigue of Aluminum Alloys

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Two commercial aluminum alloys were cyclically stressed in moist and dry air. The data obtained give substantial support to the hypothesis that variable cracking of the surface oxide is responsible for environmental fatigue effects. Processing in kerosene was found to have differing effects on the two alloys. A polar organic compound added to kerosene produced a significant reduction in the scatter of data from one alloy.

Introduction

ALTHOUGH the ultimate strength of a structural material is the mechanical property most commonly quoted, it is of less significance when considering dynamically loaded structures. In such applications the fatigue strength is the material property on which much design analysis is based. For this reason, fatigue has been actively studied for more than half a century and knowledge in this field is now accumulating very rapidly. One of the earliest findings was the recognition that there is an intimate relationship between fatigue behavior and external corrosive action, and corrosion fatigue is now well documented in most areas where direct corrosive action takes place.

In addition to obvious corrosion, it was soon realized that variations in the atmosphere itself could, in some circumstances, have a marked effect on the fatigue properties. In some of the earliest work, Gough and Sopwith¹⁻³ evaluated the results of fatigue tests carried out on several metals in a variety of atmospheres. On a nonstatistical basis, the conclusion was reached that an improvement in fatigue endurance in dry environments was due to the absence of water vapor, which, in conjunction with oxygen, had a deleterious effect on fatigue life.

Environmental effects have been clearly demonstrated for many metals, but the magnitude of the phenomenon is most pronounced in aluminum and its alloys. As most aeronautical structures are, at present, based on such materials, the significance of atmospheric effects cannot be overemphasized. In spite of this fact and the early definition¹⁻³ of many qualitative aspects, there have been few systematic investigations of direct atmospheric effects, and much of the data now available has resulted from work carried out in related fields of fatigue research. Among the systematic studies of particular interest is the quantitative analysis of Liu and Corten.⁴ It was found that the fatigue endurances of 2024-T4 and 7075-T6 aluminum alloy sheet were consistently lower in the summer months than in the winter. They were able to relate these variations to the water content of the atmosphere. It must, however, be pointed out that these data related to stress levels which were relatively high and above those which would normally be considered in designing a cyclically stressed structure of these materials.

Broom and Nicholson⁵ carried out a major study of various age-hardened aluminum alloys. They reached the conclusion that water vapor was the only significant atmospheric constituent which influenced fatigue properties. A mechanism was proposed which involved reaction of water vapor with the free surface of the metal, which had been exposed through

a crack in the surface oxide film. The crack in the surface oxide was postulated to be caused by slip in the base metal. It was also suggested that the environment influenced crack propagation as well as the actual initiation process. The influence on propagation was subsequently confirmed by detailed studies on clad 2024-T3 alloy sheet,⁶ and on clad DTD 5070A and unclad DTD 683 alloys.⁷

Although the crack-propagation phases of the fatigue process are of major importance, particularly in assessing the residual life of structural components, the basic problem is still that of initiation of the crack. It is generally accepted that fatigue failures originate at or close to the surface and, therefore, any environmental effect should be related to processes at the surface. Whereas the surface oxide was discussed by Broom and Nicholson⁵ as a requisite part of the effect, it was not considered as the direct cause of environmental variations. Liu and Corten⁴ found that a coating of petroleum jelly (vaseline) virtually eliminated variations in endurance; however, the mean value for test-pieces so coated was comparable to that of uncoated samples tested in an environment of intermediate humidity. From this data, it should be concluded that the endurance in dry air is not an absolute value for comparison purposes, and that the fatigue properties have a direct dependence on the actual surface condition.

Increasingly in recent years, it has been realized that the environmental dependence of fatigue is only one aspect of an over-all relation between environment and mechanical properties. The role of the free surface of the metal has been studied extensively with respect to its influence on dislocation behavior,⁸ and environmental effects can, in many instances, be understood satisfactorily on the basis of dislocation interactions taking place at the surface.

In aluminum, the role of the free surface is obscured by the presence of a strong coherent oxide film. Many aluminum-based alloys are similarly covered by comparable oxide films, but differences in corrosion resistance show that modifications have taken place, presumably due to the various alloying additions. Such modifications will result in differences in the properties of the oxide. Hence, due to the coherency of the surface oxide on these materials, variable free-surface effects would be expected.

The authors have studied⁹ the fatigue properties of a work-hardened aluminum alloy (Alcan 57S) in moist and dry air. One of the interesting findings of the work was that a non-linear statistical distribution of the data, termed bimodal distribution and reported previously,¹⁰ was directly related to the environment. This bimodal behavior was noted only in tests carried out in moist air, and could be eliminated by refinishing the test pieces during the latter part of the tests. It was thus suggested that only one group of the test data, in bimodal distributions, was associated with the surface oxide film. A mechanism was discussed in which a crack in the sur-

Received October 28, 1968; revision received July 7, 1969.

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face oxide film resulted in a strain discontinuity at the surface of the base metal. The environmental variations were attributed to property differences in the surface oxide formed in environments of differing moisture content.

Subsequent work¹¹ on anodized samples of the same material confirmed that the bimodal distribution reported previously was only partly related to environmental effects, with the low-endurance group of failures being associated with environmental oxide effects. An additional conclusion was that the base or barrier layer was probably that part of the oxide film responsible for endurance variations.

By studying single crystals of pure aluminum, Grosskreutz and Bowles¹² were able to show that the rate of cyclic strain hardening is decreased by removal of atmospheric gases. This finding was interpreted on the basis of oxidation of surface steps affecting subsequent dislocation movement. Subsequently¹³ it was shown that there was an appreciable change in the mechanical properties of an aluminum oxide film when the test was carried out in vacuum, and the effect was attributed to the removal of absorbed water vapour. This finding provides some confirmation to the postulation by the authors⁹ that changes in the properties of the surface oxide are responsible for endurance variations. Furthermore, in the latter work of Grosskreutz,¹³ well-defined slip bands were observed and these were related to fractures in the surface oxide. As electron microscopic studies showed evidence of other dislocation distributions, there appears to be some measure of similarity between these results and those already discussed^{9,11} defining two separate statistical groupings for the test data.

There now appears to be sufficient evidence that the fatigue behavior of aluminum and its alloys is dependent on the properties of the surface oxide film. Most of the work carried out to date has studied simple oxidation in air of varying moisture contents. As many of the industrial applications of these materials originate from routine processing operations, the oxidation has not taken place under such simple conditions. It is the purpose of the present paper to examine certain aspects of simple oxidation, as already discussed, and to present some details of the effect of processing in kerosene.

Experimental Data

The principal material studied was a commercial half-hard aluminum-magnesium-chromium alloy, Alcan 57S. This material is the same as that used previously, and the data published^{9,11} have not shown any anomalous behavior, other than that of bimodal statistical distributions in some of the test data. The nominal composition of the alloy is listed in Table 1. Some tests were also carried out on unclad 2024-T3 sheet, U.S. Federal Specification QQ-A-355.

Test pieces were prepared from blanks, cut longitudinally in the rolling direction, by machining an 11-in.-radius toroidal test section to give a minimum width of 0.475 in. The nominal sheet thickness was 0.050 in. After machining, each specimen was solvent-degreased and polished longitudinally on all surfaces of the test section with dry 400-grit silicon carbide paper. The polishing operation was carried out without lubricant in view of an undefined effect already noted.⁴ After polishing, the samples were measured and stored in ambient air until final preparation and testing. The final preparation procedure varied and is given subsequently for each series of tests reported.

Table 1 57S alloy composition

Copper	0.10% max.
Iron + silicon	0.45% max.
Magnesium	2.2-2.8%
Manganese	0.1% max.
Chromium	0.15-0.35%
Other elements	total 0.15%
Aluminum	to 100%

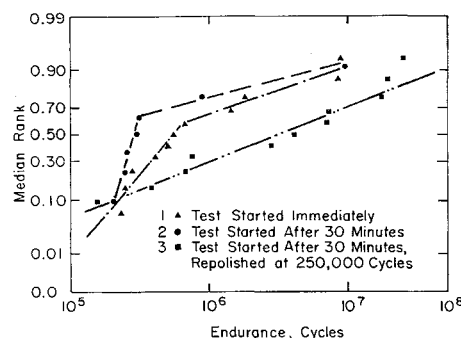


Fig. 1 Repolishing effect.

All the fatigue tests were carried out in pulsating tension with a ratio of minimum to maximum stress of 0.05. The tests reported for 57S material were carried out at maximum stress of 34,000 psi, and, for 2024-T3 alloy at 45,000 psi. Environmental control was maintained by a thin plastic bag, sealed to the grips, with a continuous flow of either moisture-saturated air or air dried with silica gel. In the latter case, the relative humidity, indicated on a sensitive laboratory instrument, was substantially less than the 5% minimum value measureable. No direct measurements were made of the various surface oxide films grown in the differing environments.

Test data were obtained either on two 2-ton Vibrophore machines, operating at 2180 cpm, or on a Sonntag SF-1 machine, operating at 1725 cpm. Calibrations were carried out prior to the investigation. Preliminary data showed that statistically the results from the two Vibrophore machines were identical, but that the data from the Sonntag machine were significantly different. Hence, no quantitative comparisons can be made between data from the two types of machines.

Results

The primary preparation of samples has already been described. For each group of test samples there was a specified final preparation. This final preparation was varied in order to produce different surface conditions.

The earlier work of the authors⁹ on 57S alloy demonstrated that holding each sample for 30 min in a moist test environment produced a noticeable change in fatigue behavior when compared to samples tested immediately, following a light refinishing operation (see Fig. 1). These data illustrate that there is some effect on endurance when there is a short interval between final refinishing and the start of fatigue stressing. To avoid this effect, therefore, in all series of tests carried out, samples either freshly refinished prior to testing or held for a considerable period to allow oxide stability to be attained, were used.

The first two series of tests were intended to establish reference curves for 57S material, in the freshly finished condition, in moist and dry environments. These data are shown plotted in Fig. 2 as median rank¹⁴ probability diagrams, assuming a logarithmic-normal distribution of data.

The next group of tests examined the effect of a stepwise increase in the oxide film during the test. Freshly finished samples were stressed in moist air for 50,000 cycles and then stored for four weeks in moist air before continuing the test to failure. The data are shown in Fig. 3, together with the outline curve for the moist-air data from the previous series.

In contrast to the data in Fig. 3, a comparable group of tests was carried out in which each sample was refinished every 50,000 cycles, to maintain a thin surface oxide. The results are shown in Fig. 4 and are not statistically different from those in Fig. 3.

These data (Figs. 3 and 4) differ sharply from those reported previously (Fig. 1), as the refinishing operation did not extend the fatigue life. The history of the samples differed

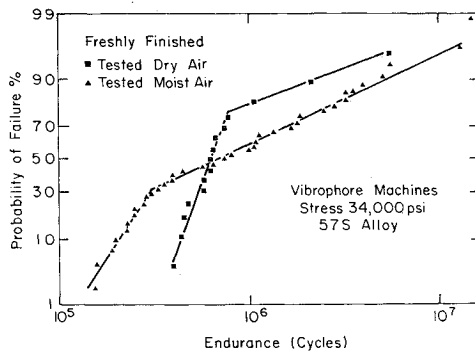


Fig. 2 Effect of environment on freshly finished samples.

in that stressing started immediately after final polishing and that the refinishing operations were carried out at 50,000 cycles. To examine these differences, tests were carried out in moist air on samples which had been stored in moist air for a minimum of three weeks between final polishing and the start of stressing. One group was tested to failure while tests on the second group were interrupted at 50,000 cycles for sample refinishing. The data are shown in Fig. 5.

The final series of tests in this group was carried out to examine the effect of an environment change during the progress of a test. Samples were freshly refinished and stressed for 50,000 cycles or 200,000 cycles in moist air. At these points the samples were refinished while still in the machine, and the tests were then continued to failure in dry air. The results are shown in Fig. 6. For purposes of clarification, Table 2 assembles the various test conditions used and the location of the data.

The preceding tests employed samples that were oxidized under strictly controlled clean conditions. Most commercial operations involve contact with various oil-base media; tests involving kerosene may, therefore, give some indications of any effects in such processing. Tests were carried out on 57S and 2024 alloys, using a Sonntag machine. Four series of tests were carried out as follows on 57S alloy:

1) The samples were polished and stored in the laboratory atmosphere for a minimum of two weeks prior to testing in moist air.

2) The samples were both polished and then stored in kerosene for a minimum of two weeks. Each sample was rinsed thoroughly in chloroethylene before testing in moist air.

3) The procedure was the same as for the preceding group with an addition of dodecyl alcohol to the kerosene (20 g/liter).

4) The samples were polished and then stored in kerosene for a minimum of two weeks. Each sample was then rinsed in dodecyl alcohol-kerosene solution (200 g/liter), rinsed thoroughly in chloroethylene, and then tested in moist air.

The data are given in Table 3 as mean values and standard deviations, both of which are calculated on the basis of a logarithmic-normal distribution of data.

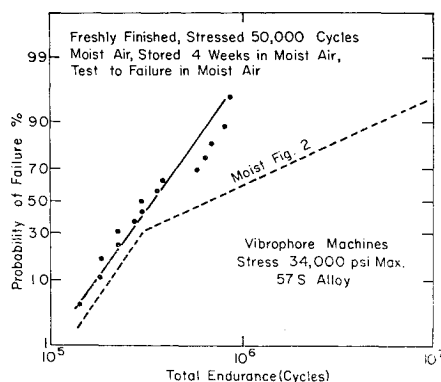


Fig. 3 Effect of an increase in oxidation after 50,000 cycles.

Table 2 Tests on 57S Alloy (Vibrophore machines)

Procedure	Data
Freshly finished, tested in dry air	Fig. 2, Curve ■
Freshly finished, tested in moist air	Fig. 2, Curve ▲
Freshly finished, stored 4 weeks after 50,000 cycles, tested in moist air	Fig. 3
Refinished every 50,000 cycles, tested in moist air	Fig. 4
Stored in moist air, tested in moist air	Fig. 5, Curve ●
Stored in moist air, refinished at 50,000 cycles, tested in moist air	Fig. 5, Curve ▲
Freshly finished, 50,000 cycles moist air, tested in dry air	Fig. 6, Curve ●
Freshly finished, 200,000 cycles moist air, tested in dry air	Fig. 6, Curve ▲

These results, for 57S alloy, show some significant variations in both the mean values and the deviation of the data. If such variations were common to all aluminum alloys, a potential would exist for the development of suitable commercial processing. Accordingly, comparable tests were carried out on samples of bare 2024-T3 material.

The four series of tests carried out were as follows:

1) The samples were polished and stored in the laboratory atmosphere for a minimum of two weeks before testing in moist air.

2) The samples were both polished and then stored in kerosene for two weeks. As for the 57S material, samples were then rinsed in chloroethylene and tested in moist air.

3) The samples were processed as for the previous group with an additional rinse of dodecyl alcohol-kerosene solution before final rinsing in chloroethylene (as for group 4, 57S alloy).

4) The procedure was the same as for group 2 except that the chloroethylene rinse was omitted and a thin film of kerosene remained on the surface after natural drainage. The data from these series of tests are given in Table 4.

Discussion

In considering the data obtained from samples of 57S alloy, oxidized and tested in dry and moist air, it is apparent that the refinishing effect, Fig. 1, is dependent on the surface condition of the material at the start of the test. The data in Fig. 1 were interpreted⁹ on the basis that the surface oxide film had no influence during the latter stages of the fatigue process. The removal of the oxide film and regrowth of a thinner film on samples already cyclically strain-hardened gave results which apparently belonged to the secondary statistical distribution. The data obtained in the present study show the opposite of this finding, provided that the samples are freshly finished prior to testing, and then progressively repolished every 50,000 cycles during the test (Fig. 4). If samples were oxidized prior to testing, an intermediate refinishing had the same effect as reported previously (Fig. 5).

Table 3 Results of tests in moist air on 57S alloy samples groups 1 to 4 (Sonntag machine)

Preparation	Number of tests	Mean endurance (as log ₁₀)	Standard deviation
1) Polished and stored in air	14	5.4143 (260,000 cycles)	0.14
2) Polished and stored in kerosene	15	5.2721 (187,000 cycles)	0.12
3) Polished and stored dodecyl alcohol-kerosene	15	5.2825 (192,000 cycles)	0.07
4) Polished and stored in kerosene, rinsed dodecyl alcohol	7	5.2744 (188,000 cycles)	0.07

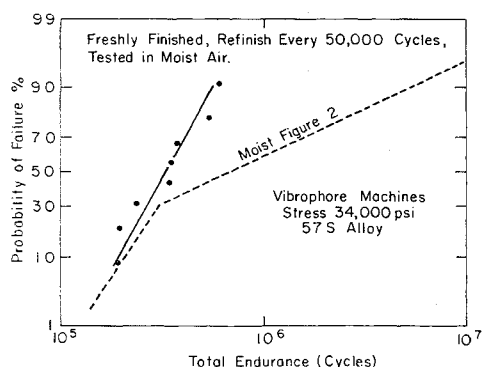
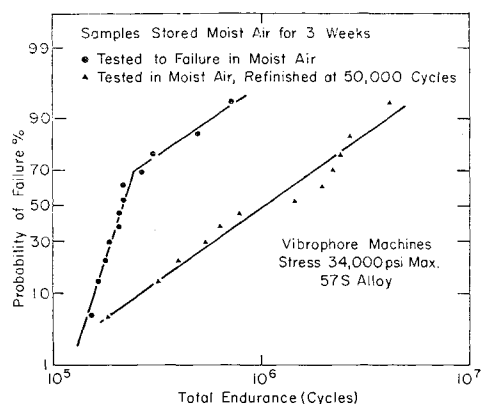
Table 4 Results of tests in moist air on 2024-T3 alloy samples groups 1 to 4 (Sonntag machine)

Preparation	Number of tests	Mean endurance (as log ₁₀)	Standard deviation
1) Polished and stored in air	9	5.4720 (296,000 cycles)	0.30
2) Polished and stored in kerosene	9	5.5362 (344,000 cycles)	0.31
3) Polished and stored in kerosene, rinsed docecyl alcohol	9	5.1120 (129,000 cycles)	0.28
4) Polished and stored in kerosene, drained only	9	5.6651 (462,000 cycles)	0.20

Considering the data for samples progressively refinished during the test (Fig. 4), it will be noted that the low-endurance values are comparable to those obtained by continuous stressing to failure. Hence, the progressive refinishing operations have increased the probability of failure beyond the point at which the probability of a second-mode failure would have otherwise become the dominant factor. This shows that stressing a freshly growing oxide is more damaging initially than after a short period during which further oxidation has taken place. In effect, each refinishing operation during the test has reactivated this damage mechanism to extend the probability curve.

An exactly similar effect has been produced by allowing a step-wise increase in the oxide film to take place at the same point, 50,000 cycles, during each test. Hence, the damage mechanism becomes more pronounced as oxidation proceeds, leaving only an intermediate stage of oxidation when extensive second-mode behavior is likely to occur. As most of the fatigue tests commonly carried out employ samples already oxidized to a substantial degree, it is probable that second-mode behavior may not have been established in many instances. In this respect it should be noted that the second mode corresponds to an increased fatigue strength, and it thus seems very probable that the low ratio of accepted fatigue strength to ultimate strength for many aluminum alloys is due to the absence of secondary-mode, or base-metal, failures in tests used to establish the fatigue properties.

Although the data in Figs. 3 and 4 seem to show that the degree of oxidation after 50,000 cycles has no noticeable effect, this interpretation is not correct. The endurance behavior of samples stressed continuously to failure (moist, Fig. 2) exhibits the secondary-mode behavior already discussed. Hence, as the oxide grows, there is first a reduction in the damage potential and then an increase as stable thickness is obtained (Fig. 3). This conclusion is in agreement with the observation that a thicker stable oxide (Fig. 5) results in a significantly reduced endurance. The implication is, therefore, that the damage mechanism loses its effectiveness as time progresses and then regains its effectiveness again as the

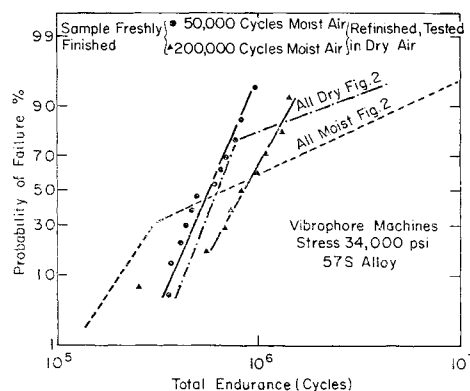
**Fig. 4 Effect of refinishing every 50,000 cycles.****Fig. 5 Effect of refinishing stored samples.**

thickness of the oxide increases. If the damage mechanism is as initially proposed,^{9,11} namely an oxide crack producing a strain discontinuity across the oxide-metal interface, then the continuing oxidation of freshly finished samples will likely repair the damage in the film fairly rapidly. At later stages when the oxide has increased in thickness, the greater differential strains across the interface will increase the amount of cracking and thus enhance the damage mechanism.

The data discussed thus far have related to tests carried out entirely in moist air. When the data in Fig. 6 are studied it can be seen immediately that a simple oxide mechanism such as discussed is not wholly valid. It should be noted that 50,000 cycles in moist air followed by refinishing have produced approximately the same damage as the same number of cycles in a continuous test in dry air. This result is contrary to what would be expected considering the data in Fig. 2, unless the damage in moist air is different or nonadditive to that taking place in dry air. When prestressed for 200,000 cycles in moist air, a net increase in total life was recorded, except for one specimen which broke very shortly after the prestress period. Such an increase in life would only occur if the damage produced in moist air has impeded the development of further damage in dry air.

An hypothesis of different damage effects in moist and dry air is not unreasonable and is in fact compatible with the oxide-crack proposal. Hydration of the surface oxide on aluminum has long been known, and measurements on the thicknesses of aluminum oxide films¹⁵ have shown a marked kinetic difference between films grown in dry and moist air. The recent work of Grosskreutz¹³ has demonstrated variations of modulus and, therefore, it would be surprising if the damages occurring in moist and dry air were identical.

The foregoing discussion places considerable emphasis on the initial stages of growth of the surface oxide. This is a natural corollary of the dependence of the process on the mechanical properties and the coherent nature of the oxide.

**Fig. 6 Effect of moist air damage on subsequent fatigue life.**

Thus, variations in the growth conditions can be reflected by the subsequent fatigue behavior. The subsequent data, listed in Tables 3 and 4, show that such oxide variations are not limited to direct atmospheric effects. As oxidation is merely a simple chemical reaction at the surface, changes in the oxidant or the presence of other chemically active materials can result in differences in the surface oxide. As an extreme example of this, the amalgam effect of mercury so alters the oxidation characteristics as to eliminate the self-healing properties of the oxide.

It is, therefore, reasonable to assume that preparation and storage in kerosene have resulted in some modifications to the surface oxide. Such modifications are in fact indicated for 57S alloy by the reduced mean endurance of samples so treated. The reductions noted in Table 3 are statistically significant to a confidence of 99.5% or better. Processing in kerosene-dodecyl alcohol solution has similarly reduced the endurance and has also substantially reduced the spread of the data. The reduction in scatter is significantly reduced in respect to both processing in air (>97.5% confidence) and in pure kerosene (>95% confidence). This reduction in scatter is not, however, related to processing in contact with dodecyl alcohol as a simple rinse treatment before testing produces a similar reduction. Therefore, in this instance, the effect of dodecyl alcohol probably takes place at the outer surface of the oxide rather than at the interface between the oxide and the parent metal.

Kerosene processing and contact with dodecyl alcohol have had strikingly different effects on 2024 alloy. In this case, processing in kerosene has had no significant effect on the mean endurance or the scatter of the data, but contact with dodecyl alcohol has significantly reduced the mean endurance, without significantly affecting the scatter. This difference in behavior between two alloys is of considerable interest. It demonstrates that generalization cannot and must not be made in predicting the behavior of one material on the basis of the performance of another, even if closely related.

The variable performance of these two alloys can be compared with the data reported by Frankel, Bennett, and Holshouser.¹⁶ These workers studied, among other materials, an age-hardened aluminum alloy, 6061-T6, and found that coating with dodecyl alcohol had no effect on either the mean or the scatter of the data. However, for an alloy steel, a magnesium alloy, and beryllium copper, increased endurances and reduced scatter were found. It therefore appears that dodecyl alcohol has a highly variable effect on fatigue properties depending on the material studied. As a surface interaction is indicated from the data on 57S alloy, an assumption is that the effect of dodecyl alcohol is related to modifications of the surface oxides on the various aluminum alloys.

In summary, the conclusions drawn from the work reported are as follows:

1) For atmospheric oxidation of 57S aluminum alloy, the fatigue damage that takes place in moist air is different and nonadditive to that taking place in dry air.

2) Processing in kerosene has different effects on 57S and 2024 aluminum alloys. Similarly, contact with dodecyl alcohol has different effects on the two alloys. With 57S alloy, dodecyl alcohol reduces the scatter but has no effect on the mean endurance, whereas for 2024 alloy the endurance is reduced with no effect on the scatter.

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