PROCEEDINGS OF THE MEETING OF THE MECHANICAL FAILURES PREVENTION GROUP (17th) HELD AT THE NATIONAL BUREAU OF STANDARDS, BOULDER, COLORADO ON 25-27 APRIL 1972

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**Title:** Proceedings of the 17th Meeting of the Mechanical Failures Prevention Group  
April 25-27, 1972

**Abstract:**
Report of three-day discussions by a group of nationally-recognized specialists of the subject "Environmental Effects on Mechanical Failures, Mechanisms and Detection." Summaries are presented of fifteen prepared talks which had as their objectives the examination of the state of the art on various aspects of environmental effects on mechanical failures, the mechanisms involved and the methods of detection. Limitations and gaps on the technology available for problem solving are identified, providing guidance for future research. Reports of problems encountered in current field service provide an estimate of the magnitude of the problem and the relevance of current research. Significant audience discussions are reported.

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MINUTES OF 1/TH MEETING OF THE MECHANICAL FAILURES PREVENTION GROUP, A COORDINATED PROGRAM FOR ANALYSIS, DETECTION, AND CONTROL OF MECHANICAL FAILURES, HELD AT THE NATIONAL BUREAU OF STANDARDS, BOULDER, COLORADO ON APRIL 25 - 27, 1972

ATTENDANCE: (See APPENDIX I)


SUMMARY: Attention was centered at this meeting upon the EFFECTS OF ENVIRONMENT UPON MECHANICAL FAILURES, MECHANISMS, AND DETECTION. Stress corrosion cracking and lubrication failure were among the environment-sensitive failure modes to receive attention in the technical program of fifteen prepared presentations and concurrent general discussion. Opportunity was provided for inspection of the laboratory facilities at N.B.S. Meetings of each of the four MFPG Technical Committees, as well as the Steering and Government Representatives Committees, were held in conjunction with the open sessions. A social evening was provided to foster individual acquaintances. The host for the meeting was the National Bureau of Standards.

INTRODUCTION: The Seventeenth Open Meeting of the MFPG was called to order at 1 p.m. on April 25, 1972 by Mr. S.W. Doroff of the Office of Naval Research, MFPG General Chairman. Noting that this meeting of MFPG coincided very closely with its fifth anniversary, he introduced Dr. R.H. Kropshot, Associate Chief of the Cryogenics Division of N.B.S. Boulder Labs. Dr. Kropshot outlined the scope of the technical laboratory activities of the 600-man N.B.S. staff at Boulder and extended a cordial welcome to the MFPG on behalf of Dr. Birmingham, Deputy Director. Mr. Doroff next introduced Commander C.R. Oberg, USN, Director for the MFPG Program for ONR in Washington.
CDR. Oberg noted that, following the present meeting, sponsorship of the MFPG would be transferred (on July 1, 1972) to the National Bureau of Standards. Since its inception, MFPG has expanded its horizons far beyond the military interest, becoming a truly national effort. Association with the Failure Avoidance Program of the NBS is a natural and constructive step. MFPG has already had an important impact upon practices within the Navy, and practices in industry also reflect the contributions of MFPG discussions. Closer relationships between representatives of the many interested government agencies and the MFPG Steering Committee is indicated in the future. Dr. Passaglia was identified as the new Executive Secretary of MFPG. Noting his strong conviction of the important role which MFPG has to play in the technological future of this country, CDR. Oberg thanked the members of the Steering Committee, Drs. Sternlicht, Ling, Gross, Gatts, and Sawyer, for their individual contributions in bringing the problem of mechanical failure prevention into the national awareness, and predicted accelerated progress for the work in its new administrative framework.

Mr. Doroff then introduced Dr. Elio Passaglia, Chief of the Metallurgy Division of the Institute of Materials Research, NBS, as Chairman of the first technical session to follow. The summaries of speakers' remarks which follow were furnished by the speakers themselves unless otherwise noted. (Readers interested in more detailed information are encouraged to correspond directly with the speakers.) Audience discussions are reported by the administrative staff; the Executive Secretary will appreciate learning of substantive errors so that they may be corrected.

1. " ADSORPTION-SENSITIVE FRACTURE OF SOLIDS," by A.R.C. Westwood, Director, Research Institute for Advanced Studies, Martin Marietta Corporation, 1450 South Rolling Road, Baltimore, Maryland 21227.

Some of the most fascinating and potentially useful effects of environments on mechanical behavior of solids occur as a consequence of the adsorption of surface active species. Such effects arise because adsorbates can influence (i) near-surface flow behavior, especially of nonmetallic solids, and so affect the failure controlling crack initiation step in these notch-sensitive materials, (ii) the cohesive energy of surface bonds, and so crack propagation behavior - especially the rate of sub-critical crack growth, and (iii) the kinetics of corrosion processes, allowing inhibition of corrosion and stress corrosion cracking (SCC).

As discussed at an earlier MFPG Meeting (1), the influence of adsorbates on mechanical behavior can sometimes be understood, conceptually at least, in terms of the adsorption-induced redistribution of charge carriers in the near-surface regions of the solid, and of the effect of this redistribution on near-surface flow behavior. This concept is especially applicable for ceramics, glasses and rocks. For metals, of course, the high concentration of mobile electrons screens out the influence of any adsorbate within a few angstroms of the surface. Thus, ordinarily, the macroscopic flow behavior of a metal is relatively insensitive to the presence of adsorbed species. However, when the energy to form surface steps is a significant factor in determining the mobility of near-surface dislocations - as it is, for example, when indenting the basal plane of zinc monocrystals, - then adsorbed species can have a significant effect on microhardness, e.g., causing
variations of up to 50%. This phenomenon, the electrocapillary effect, may find useful application in the machining of nickel-base superalloys (2).

Nevertheless, it is usually the fracture behavior of a metal, rather than its flow behavior, which is most environment sensitive. The phenomenon is liquid metal embrittlement (LME) probably the most spectacular examples of adsorption-sensitive fracture in this class of solids. Recent studies have shown that this phenomenon is by no means as 'specific' as previously thought. Many elements can be embrittling, providing the right conditions of temperature, concentration of active species, and grain size, etc., are met. Possible ways of controlling this deleterious effect are (i) by adjusting the composition of the liquid phase, adding elements known to form stable compounds with the solid metal, and so "brazing" together incipient cracks, (ii) by alloying the solid metal with elements known to form stable compounds with the embrittling liquid phase (usually substantial additions are required to produce significant effects), and (iii) by changing the operating temperature - LME is extremely temperature sensitive, see Fig.1 (3).

For non-metals, on the other hand, the influence of electrically active adsorbates can extend several microns into the solid, and if its charge carriers are ions of sufficient mobility, then their redistribution can lead to substantial changes in near-surface flow behavior. Now, the charge carriers in soda lime glass are Na⁺ and possibly, either OH⁻ or O₂⁻, and it may be that the adsorption-induced redistribution of these species is responsible for the spectacular effects of the n-alcohols, etc., on the hardness and machinability of this material. For example, heptyl alcohol produces a 25% increase in hardness and a 20-fold increase in the rate of drilling with a diamond bit of soda lime glass over that in water, Fig.2 (4).
Such effects have been found to be related to the surface charge on the glass (5). Soda lime glass is hardest at its zero point of charge, and any environment which can produce zero surface charge in the dynamic situation of machining will optimize cutting efficiency for an impact type of bit. [The mode of cutting action of the bit is very important (6). For a review of environment-effects on the hardness of non-metals, see Ref. (7).]

![Fig. 2](image)

**Fig. 2** EFFECTS OF ENVIRONMENT ON (a) DRILLING RATE AFTER 200 sec WITH A DIAMOND BIT, $D(200)$ AND (b) PENDULUM HARDNESS (PHN), $O$ OF A SODA LIME GLASS. $N_C$ IS THE NUMBER OF CARBON ATOMS IN THE MOLECULE (4).
Environments can, by affecting near-surface flow processes, also markedly influence the rate of sub-critical crack growth in glass, and hence - presumably - influence delayed failure in this material. Experiments to investigate this possibility, using "center-loaded crack" specimens, have revealed that even such relatively inert environments as tetradecane can markedly reduce the energy required to propagate a slowly moving crack in glass; see Fig.3 (5). At this time, it is presumed that tetradecane is so effective because it induces a significant positive charge on glass, softening it locally (see Fig.2), and so facilitating 'ductile' crack growth.

Adsorbates can also be used to control corrosion and stress corrosion processes, one example of such behavior being illustrated in Fig.4 (8). In this case, the caustic embrittlement of mild steel, which is particularly severe at an applied potential of -950 mV, is completely inhibited by the addition of, for example, 15 w/o of valonea.

Fig.3 INFLUENCE OF ENVIRONMENT IN THE ENERGY ($\Phi_p$) REQUIRED TO PROPAGATE A STABLE (SUB-CRITICAL) CRACK IN A SEMI-BRITTLE MANNER IN SODA LIME GLASS (5).
The technological potential for the application of the effects of adsorbed species on mechanical behavior is extremely exciting. Some obvious applications include:

(i) Enhanced drilling rates for tunneling through hard rock for rapid transit, utility and defense systems, etc. Work at RIAS has already demonstrated three-fold increases in drilling rate over that in water for granite in lab scale tests (7, 9).

(ii) Enhanced machining rates for metals (superalloys) and hard ceramics. Preliminary studies at RIAS (9) indicate that 4 - 5 fold increases in the rate of drilling of alumina are possible, and when it is appreciated that the cost of grinding an alumina substrate can represent 60% of the cost of a microelectronic component, clearly the potential for cost reductions here are substantial.

(iii) Improvements in the efficiency of comminution processes. Comminution is an extremely inefficient process (~1%), and yet it represents, for example, some 15% of the manufacturing cost of cement, and perhaps a higher precentage of the cost of producing aggregate. With power costs increasing rapidly, a study of ways of utilizing active chemical environments to facilitate the comminution process (as well as to act as dispersgents) should be undertaken, and better ways of comminuting other than the convential 'violent impact' approach should also be sought.

(iv) Possible control of fluid-injection induced earthquakes via control of the frictional behavior of the rocks impinging across the fault (10).

(v) Development of superior lubricants, formulated to harden (?) the oxide films protecting the moving parts, and so reduce wear and failure rate.
(vi) Increased use of inhibitors for corrosion and SCC.

Unfortunately, very little R&D effort is currently being applied to this area in the United States - in contrast, say, to the U.S.S.R. or West Germany. An integrated program of imaginative science and innovative technology on adsorption-sensitive flow and fracture behavior could prove to be one of the most cost effective investments the U.S. Government could make at this time.

REFERENCES


DISCUSSION - Grosskreutz noted that some glasses show a maximum surface free energy around a chain length of 7 or 8, and asked how that could be reconciled with the fact that cutting rate is highest at that point. This brought the significant reminder that consideration of the whole system of solid, environmental liquid, and cutting tool action made the situation rational. Tools in general cut by either a "plowing" or "rapid impacting" action; the former (used with aluminum) cut faster when the surface is softened, while the latter do best when the surface is most brittle. The tool action in Fig.2 was that of an impact-type (diamond bit) tool, and was most effective when the glass was hardest. The speaker could give Miller no rigorous explanation of the mechanism through which the environmental fluid produces the observed effects, or why the chain length of
alcohol should influence them; more investigation is needed. It was agreed that a surface electric field would have the same initial effect as some of the charge-altering fluids; however, as a crack propagated inward it would rapidly escape the electric field, while the adsorbent liquids would follow along with the crack tip. There is a valuable flexibility in the freedom of choice of adsorbent liquids and liquid mixtures to produce any desired characteristics. Thompson felt intuitively that some kind of surface chemistry effect must occur at the crack tip; Westwood conceded that there was no evidence that there was not such an effect.


The strength of glass is controlled by the distribution of cracks within the glass surface and the growth of these cracks under imposed load. Surface cracks are introduced accidentally when glass is handled or during finishing procedures, and failure occurs when the crack tip stress exceeds the theoretical strength of the material. If a corrosive environment is present, crack growth and failure occur at a much lower stress as a consequence of reaction between the corrosive environment and the highly strained material at the roots of the crack tips. This process leads to a time delay to failure, the time delay being equal to the time necessary for cracks to grow from subcritical to critical size. This process is called static fatigue and normally results from a reaction between glass and water in the environment (1-6). Studies of static fatigue indicate that the time delay to failure is absent in dry environments. Propagation of cracks in glass depends on the relative amounts of water in the environment and upon the temperature to which the glass is exposed. Fracture mechanics techniques can provide information on the response of cracks to stress, temperature and environment (6). These techniques are also useful for design purposes.

The technique most widely used to obtain fracture mechanics data on glass is the double cantilever cleavage technique. Specimens consist of glass microscope slides, 1 inch by 3 inches in each side and 2 mm thick, Figure 1. The midplane of the specimen is notched to provide a guiding path for the crack. The crack velocity studies can be conducted in either gaseous or liquid environments and the chemical composition and temperature of the environment can be controlled. Thus, it is possible to study the effects of glass and environment, composition, temperature and applied load on fracture. Crack velocity studies are usually made using either a dead weight loading system or a universal testing machine for application of load, and crack velocity measurements ranging from $10^{-3}$ to less than $10^{-11}$ m/s have been obtained.

An example of the type of data obtained by this technique is given in Figure 2. Here, the fracture behavior of four glasses in water at 25°C was investigated. Composition is shown to have a marked effect on the rate of crack growth. Data for soda lime silicate glass and borosilicate glass indicate an exponential dependence of stress intensity factor on crack velocities greater than $10^{-7}$ and $10^{-8}$ m/s, respectively. At slower crack velocities, the crack velocity decreases at greater than an exponential rate, suggesting a threshold stress below which crack motion will not occur. This threshold is known as the static fatigue limit.
Fig. 1 SAMPLE CONFIGURATION. P IS THE APPLIED FORCE, L IS THE CRACK LENGTH, AND \( w \) AND \( t \) ARE SPECIMEN DIMENSIONS.

Fig. 2 EFFECT OF GLASS COMPOSITION ON CRACK PROPAGATION RATE. TESTED IN WATER AT 25°C.
Aluminosilicate and silica glasses differ from the other two since the behavior is exponential over the entire range of experimental variables. There is no indication of the static fatigue limit although one presumably exists at lower stress intensity factors. Crack propagation techniques can also be used to show that fracture is an activated process and depends on the pH of the electrolyte in which the test is conducted (7,8). In gaseous nitrogen, the fracture of glass depends also on the amount of moisture in the gaseous environment (9).

Crack velocity data can be used to obtain estimates of survival time for glass under load. Two methods of estimation will be discussed. The first assumes that flaw size distributions have been obtained for the glass. The second uses a proof test to determine the maximum flaw size that could have been present on the glass surface prior to use. In each method the time to failure can be calculated from the initial flaw size and the crack velocity data.

The total time to failure can be determined from the definition of crack velocity, \( \frac{dL}{dt} = v \), and the assumption that the stress intensity factor, \( K_I \), is related to the applied load, \( \sigma \), by the following equation,

\[
K_I = \sigma \sqrt{\pi L},
\]  

(1)

where \( L \) represents the depth of the surface crack. This equation is approximately correct for cracks that are small with respect to the plate thickness and for which the length of the crack on the surface is much greater than its depth. Assuming a constant load, the following equation for total failure time, \( t \), is obtained by substituting Eq.(1) into the definition of crack velocity (10).

\[
t = \frac{K_{IC}}{2(\sigma^2 \pi)} \int_{K_I}^{\infty} \left( K/I \right) dK
\]

(2)

where \( v \) is the crack velocity and \( K_I \) is the stress intensity factor calculated from the initial crack length and applied load.

Equation (2) can be integrated either numerically or analytically provided \( v \) is known as a function of \( K \). For much of the data obtained on glass, the crack velocity is found to be exponentially dependent on the applied stress intensity factor,

\[
v = v_o \exp \beta K_I.
\]

(3)

Substituting Eq.(3) into (2), the following integrated expression for failure time is obtained provided small terms are neglected,

\[
t = 2L/\beta K_I v_o \left[ \frac{1}{(\beta v_o \sqrt{\pi} \exp \beta \sigma \sqrt{\pi L})} \right].
\]

(4)
where $v_1$ is the initial crack velocity corresponding to the initial stress intensity factor $K_1$. This equation has been checked with numerically integrated times-to-failure using the actual crack velocity curves and agreement was excellent over the entire practical range of crack growth (7).

The time to failure depends only on the applied load $\sigma$ and the initial crack length $L_1$. The other terms of the equation are constants obtained from crack velocity data. If the initial flaw size is known, Eq.(4) provides a unique relationship between applied load and time to failure, and is of course the equation needed for design purposes. For safe design, the initial flaw length, $L_1$, selected for Eq.(4) should be larger than flaws actually occurring in the glass surface. This procedure will guarantee a greater time to failure than calculated from Eq.(4).

Statistical information on flaws contained in a glass surface can be obtained from strength measurements under very dry conditions such as liquid nitrogen where stress corrosion does not occur (11). The statistical information can be used to select a safe initial flaw size for substitution into Eq.(4)*. The probability of the glass containing flaws larger than that selected gives the probability of failure in a time less than that calculated from Eq.(4). The statistical estimation of flaw severity should be typical of those expected for plates in service for this method to be of value. The method also cannot guarantee that the flaw distribution has not been altered by accidental mishandling of the glass.

Proof testing can be used to eliminate weak glass plates and to estimate the largest possible flaw in the plates at the time of testing. Survival of a proof test guarantees that the stress intensity factor of the most serious flaw in the glass plate has not exceeded $K_{IC}$ since fracture is almost instantaneous when

$$K = K_{IC}.$$ The maximum flaw length contained in the glass surface is given by

$$L_1 = \left(\frac{K_{IC}}{\sigma_p}\right)^2,$$

where $\sigma_p$ is the proof test stress. The minimum time to failure can be calculated from Eq.(4). Greater safety at operating stresses is obtained by proof testing guarantees a minimum lifetime at the time of the test, it loses value if subsequent surface damage is incurred.

In summary, a discussion has been presented on the use of fracture mechanics data to predict survival time under load. This technique is useful for two purposes: (1) for evaluating of the fracture resistant properties of different glass compositions, and (2) for development of tests to be used to assure the survival of glass under load. Further research is necessary to fully equate the time-dependent properties of investigations of the flaw structure of glass as introduced by normal handling procedures and by grinding and polishing procedures used to finish glass surfaces. Relationships between the flaw damage normally present in glass surfaces and the stress intensity factor existing at the tips of flaws will be necessary to use the above equations.

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* Equation (4) applies to a glass body under uniform surface tension. For pressure loaded plates, the variation of surface stress across the plate surface would have to be taken into account.
REFERENCES


DISCUSSION - The use of the term "stress corrosion cracking" with reference to delayed failure of glass was indicated to reflect the speaker's acceptance of the theory of occurrence of a chemical reaction between water and glass in the highly stressed region at the crack tip. If this stress-enhanced chemical reaction does in fact occur, then "stress corrosion cracking" is an appropriate term. However, "static fatigue" is the term usually used; the speaker considered the terms synonymous. There was some discussion of the application of the time to failure equation to practical problems such as window glass and pressurized glass containers, where proof testing can be most useful. Some further details of the test techniques used in the fracture mechanics of glass were described.

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3. "ROLE OF CORROSION IN BOUNDARY LUBRICATION," by E.E. Klaus, Professor of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802.

A modern mechanistic picture of boundary lubrication, particularly in steel bearing systems, appears to consist of a sequential three-step process. In the first step, polar molecules from the lubricant are adsorbed on the solid bearing surfaces. The
second step involves a chemical reaction between the adsorbed layer and the solid surface. The energy source for the reaction is frictional heating which may be aided by a catalytic effect of the solid surface, thereby lowering the activation energy of the reaction. Physical contact between the solid asperities does not appear to be a basic requirement for this chemical corrosion or erosion reaction. The final step in the sequence is the removal of the corrosion product by the high shear forces at the bearing surface or by cavitational effects as the solid surface leaves the concentrated contact. The removal of the corrosion product leaves the surface free to repeat this process again. The relative reaction rates in the corrosion step and the relative tenacity in the removal step appear to be important steps in many modern bearing applications.

Most lubricants contain a variety of impurities and additives that fulfill the role of polar materials for the adsorbed film. Preferential adsorption determines which of the polar materials dominates in the corrosion reaction (1,2).

The development of super-refined mineral oils in which the polar impurities have been reduced to a few parts per million has been the key to the study of the effect of specific additives or polar impurities (3,4). In a typical conventionally-refined mineral oil, polar impurities containing sulfur, oxygen, or nitrogen may range from less than 1 to greater than 10 percent. Aromatic hydrocarbons also appear to be more polar than the saturated hydrocarbons present in the super-refined mineral oil. In the absence of these polar materials in the hydrocarbon (mineral oil), dissolved oxygen from the air is an effective lubricity additive (5). The effectiveness of dissolved oxygen as an antiwear additive in a super-refined mineral oil (MLO 7470) appears to vary with concentration when evaluated in a four-ball wear tester as shown in Figure 1. The increase in wear below the minimum effective oxygen concentration represents a scuffing or seizure type failure. The wear level appears to be dependent upon load but independent of bulk oil temperature over the range of 167° to 400°F. It has been suggested that the wear in this case is simply a function of the reaction of the iron on the surface with oxygen dissolved in the fluid to form an iron oxide (6). Recent studies show that in all cases there is a significant reaction between the metal and a component of the liquid to produce a soluble as well as an oil insoluble organometallic reaction product (7). This organometallic product appears to be involved in the surface film formation along with the iron oxide. In fact the oil insoluble organometallic material is a varnish-like product and may influence significantly the resistance to removal of the reacted product on the surface by shear and/or cavitational forces. The same type of organometallic products are formed in static high temperature oxidation and thermal stability tests in the presence of steel surfaces (8). In these static tests a strong affinity of the organometallic product for the surface of the metal has been shown. In fact, in many cases the layer of organometallic material adsorbed on the metal surface reduces further corrosion of the metal surface to a very low level. A similar level of organometallic (pyridine soluble) product appears to be formed by the super-refined mineral oil in wear tests conducted under an air or nominal nitrogen atmosphere. The large difference in chemical reactivity appears to be a function of the amount of dissolved oxygen available. The high levels of available oxygen produce what appears to be corrosive wear, probably due to the ease of removal of the surface reaction product. At low oxidation levels, the easily sheared film appears to be more tenacious. On the other hand, at low levels of dissolved oxygen a breach of the easily sheared
Fig. 1 EFFECT OF DISSOLVED OXYGEN ON THE WEAR BEHAVIOR OF A SUPER-REFINED MINERAL OIL
Fig. 2 EFFECT OF SEVERAL DISSOLVED GASES ON WEAR BEHAVIOR
film results in a scuffing type failure due to the lower level of reactivity in forming a new film on the metal surface. This series of experiments illustrates the two important chemical corrosion or erosion reactions that appear to dominate wear in the so-called "nonreactive lubricants." Rather than nonreactive, these lubricants could be adequately described as liquids containing ingredients that are less effective as lubricity additives than is dissolved oxygen.

A similar case can be made for competing surface reactions in the study of tricresyl phosphate as the lubricity additive in super-refined mineral oil. In this series, the quantity of acid phosphate impurity in the tricresyl phosphate assumes the role of the lubricity additive (1,2) which reacts with the steel surface in competition with the formation or organometallic deposit from the super-refined mineral oil-metal reaction product.

Tests to determine the effectiveness of dissolved gases from the gaseous environment in contact with the liquid lubricant have been conducted in the same manner as those using oxygen (9). These gases include helium, argon, nitrogen, carbon dioxide, hydrogen sulfide, and dichlorodifluoromethane. In all cases the amount of gas dissolved was measured by gas chromatographic techniques. These techniques are sensitive enough to measure trace solubility of oxygen down to the order of 0.2 part per million by weight. Helium, nitrogen, and argon all appear to be inert in these wear studies. However, contamination with small quantities of oxygen or air appears to be inevitable. As a result, the tests with these three inert gases merely show the effect of the small concentrations of oxygen carried along as an impurity.

Tests run under atmospheres of CO₂, H₂S and CCl₂F₂ show distinctive wear behavior indicative of the major gas present. In these cases there is no indication that the very small traces of oxygen present had any influence on the surface chemical reactions (corrosion). These three gases show some level of increased corrosion activity with increased bulk temperature as shown in Figure 2. These gases, however, show no indication of reaction with the super-refined mineral oil. A true concentration versus wear picture has not yet been obtained for these gaseous lubricity additives because of the problems of controlling oxygen impurity levels in multiple component gaseous systems.

These data confirm the fact that the gaseous atmosphere in the lubrication system can play an important role in the boundary lubrication reaction. In many so-called nonreactive lubricant compositions, the dissolved gases from the atmosphere may in fact play the dominant role in boundary lubrication.

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DISCUSSION - Snediker's question brought out that in the case of a sealed system running on super-refined mineral oil, the choice of cover or "fill" gas is less important than the choice of lubricity additive. For the oxygen that would be in an air environment, one can substitute any additive that serves the same useful purpose. For instance, tricresyl phosphate seems to be independent of cover gas, as are esters when used as additives. Jackson suggested that the environment of a "mist" lubricating system might act differently than that of a standard force-feed or splash system. The speaker confirmed that it had the effect of making the cover gas important, since the mist ensures that the lubricant will be saturated with it. For air, the prevalence of sufficiently high temperature would produce very rapid oxidation unless well inhibited. If well inhibited, one could only guarantee operation on the high-oxygen side of the curve of Figure 1.


Failures of high strength steel in gaseous environments are commonly divided into two temperature regions; the gas-metal attack and subsequent fatigue at elevated temperatures, and the stress corrosion cracking or hydrogen embrittlement at ambient temperatures. Since the structural changes in materials during the gaseous attack at high temperatures are most severe and varied, it is generally expected that the effect of corrosion on fatigue should be large. It is known that at lower temperatures, gaseous atmospheres containing water vapor enhance brittle failure in high strength steels.
In the present work, the reaction of CO-CO₂ mixtures has been investigated in order to relate the possible effect of reactions and reaction products to the failure problems. Iron is oxidized in these atmospheres to produce a single layer of wustite. A theory has been presented by Petit and Wagner (1) for the linear to parabolic oxidation transition based on the interplay of a phase boundary reaction and volume diffusion across the oxide layer. Oxidation behavior of the steel 4330 in dry CO-CO₂ atmosphere has been studied by the thermogravimetric technique, metallographic examination and probe microanalysis.

In pure CO₂, the weight change-temperature curve exhibited a rapid gain from 1000°C, whereas only a slight gain was shown in pure CO throughout the temperature range (Fig.1). However, in the mixture gases, there were regions of a weight loss before the temperature was reached for a sharp oxidation (1200°C for CO/CO₂ = 1/1, 1300°C for 1/2 and 1/3). Metallurgical inspection of the alloy cross-section indicated that the final oxidation product consisted of three oxide layers; a compact external scale mainly of wustite, a second scale of spinel mixtures, and a zone of internal oxidation that developed preferentially along the grain boundaries.

The kinetics and mechanism of oxidation were studied at a series of temperatures from 1000 to 1300°C. Under sufficient oxygen partial pressure (CO/CO₂ = 1/1 at 1200°C and 1/2 at 1300°C), kinetics followed a linear rate law as shown in Fig.2. It appears that the phase boundary reaction at the gas-metal interface is rate-determining. In lower oxygen partial pressure, the rate exhibited a parabolic decrease at early stages of exposure, followed by a logarithmic increase. The former step is associated with decarburization through diffusion of carbon, and the latter with the growth of internal oxide zone. In the intermediate pressure (1/1 at 1000°C), a transition from logarithmic to linear was seen. The overall reaction therefore includes decarburization and both internal and external oxidation depending on the condition of oxidant.

Figure 3 shows a crack developed from the alloy surface after exposure in CO/CO₂ = 1/3 at 1100°C. It is noted that a zone of internal oxidation developed around the crack in the absence of external scale. In the process of decarburization, Oikawa et al. (2) observed that ferrite grains formed at the surface are always columnar and the α/γ interface is well-defined. The crack initiation may be produced by the surface weakening through depletion or enrichment of alloy components, and by the stress produced in the oxide zone, where the specific volume of the reaction product is much higher than that of the alloy substitute.

The second type of failure in CO-CO₂ is stress corrosion cracking at lower temperatures in the presence of moisture. It has been reported that ferritic steels are susceptible to stress corrosion cracking at room temperatures up to 100°C and a lack of one component of CO-CO₂-H₂O results in no cracking (3,4).

Preliminary experiments have been made using a U-bend specimen in an autoclave under CO 20 psi, CO₂ 100 psi and distilled water at 50°C. Intergranular and transgranular crackings observed. The cracking appears to involve hydrogen embrittlement by hydrogen liberated from the liquid condensed at the crack tip.
Fig.1 OXIDATION OF STEEL 4330 IN CO, CO₂ AND MIXTURES.
Fig. 2 OXIDATION OF STEEL 4330 IN CO/CO$_2$ AT 1000-1300°C.

Fig. 3 CRACKING OF STEEL 4330 WITH INTERNAL OXIDATION ($\times$ 100).
REFERENCES


DISCUSSION - Jackson noted the absence of any indication of serious weight loss due to iron carbonyl and direct sublimation of iron from the surface at temperatures below 600°C, peak carbonyl formation being in the 300-400°C range. He had noted its occurrence in the presence of ammonia or methanol, in fact any process where CO, CO₂ and water are present, particularly when free hydrogen was present. The speaker noted that water was not present in the tests reported.

4A. The meeting recessed at 4:55 p.m. A group dinner at 7 p.m. featured an interesting report on the role to be played by nuclear power plants in meeting the national energy crisis, and some of the problems solved and to be solved. The speaker, Mr. Ramon Hull, is a Reactor Inspector with the Denver Regional Office of the AEC. The regular meeting reconvened at 9 a.m. on April 26 for its second technical session with Lt. R.S. Miller, USN of the Office of Naval Research as Chairman.


All fatigue failures should be termed "corrosion fatigue" except those which occur in vacuum or an inert environment. However, it has been common practice in the past to use standard conditions of room temperature, pressure, and air environment as the baseline against which to measure fatigue performance. For example, the standard metallographic features of fatigue, fractographic features, and S-N curves have almost all been developed under these so-called "standard conditions". Deviations from this behavior in more aggressive environments have been commonly referred to as "corrosion fatigue". We will refer to this as conventional corrosion fatigue.

A more rational approach to the whole subject of corrosion fatigue is to consider the behavior of materials in an inert environment as the baseline and to systematically investigate the effects of other environments on the basic mechanisms of fatigue fracture, i.e., crack initiation and crack propagation. Such an approach, now in its beginning stages, allows one to understand the problem of corrosion fatigue and to select materials for resisting it more intelligently.
The main effect of environment on crack initiation is to accelerate it. Prior corrosion, in the form of pits on the surface, is analogous to notching or pre-cracking the specimen. In the absence of prior corrosion, the environment accelerates the formation of persistent slip bands and the deformation at grain boundaries which leads to fatigue crack initiation. In an experiment on pure aluminum (slip band crack initiation), the number of cycles to initiate a crack in saturated water vapor was only 60% of that required in a vacuum.

Once the fatigue process enters the crack propagation stage, all of the action is concentrated at the crack tip. Hence, the effect of environment will be measured in terms of its contribution to the crack growth rate. Figure 1 illustrates the effect of several environments on the rate of crack propagation in an aluminum alloy. The rate in dry argon (inert environment) is given for reference. As far as corrosion fatigue is concerned, the most important event at the crack tip is the creation of new surface. This point is illustrated in Fig. 2. In the case of triangular waves, where new surface is created throughout the first half of the cycle, the crack growth rate is a factor of 3 larger than for square waves for which new surface is created only during the initial rise time of the wave.

Loading frequency has a significant effect on corrosion fatigue cracking rates. The higher the frequency, the less the corrosive effect, Fig. 3. The usual explanation for this observation is that a finite reaction time exists for corrosive attack at the crack tip and if the period is shorter than this time, then the effect is diminished. Another time limiting factor is the diffusion rate of environment down the crack in order to attack the fresh surface being exposed at the tip.

The mechanism by which the environment accelerates crack growth is not clear at present, but a popular explanation makes use of the hydrogen which is released when water vapor (or other environments) cause oxidation of the metal surface:

\[ M + H_2O \rightarrow MO + 2H. \]

This hydrogen diffuses into the metal and somehow reduces the surface energy or bond strength of the metal, analogous to hydrogen embrittlement of steels.

The control of corrosion fatigue at present is, for the most part, comprised of standard "fixes" and intelligent selection of materials in the design of new structures. Introduction of compressive residual stresses at the surface is a time-honored method for reducing corrosion fatigue rates. Cathodic protection offers some reduction in fatigue crack growth rates provided the structural component is not so thick that crack tip potentials differ markedly from those at the surface. Coatings for protection against the environment are effective provided they remain intact and do not crack during the fatigue loading. Anodic coatings and electroplated coatings are notorious for cracking, in which case fatigue cracks readily initiate at the breaks in the film and fatigue is accelerated. An important parameter in this case is the fracture strain of the coating, which should always be greater than the maximum strain in the substrate. Even so, coatings extend fatigue life only in the long-life regime and the improvements there have been disappointing.
Fig. 1 EFFECT OF VARIOUS ENVIRONMENTS ON GROWTH RATE OF CORROSION FATIGUE CRACKS IN 7079-T651 ALUMINUM.
(FROM SPEIDEL, BLACKBURN, BECK AND FEELEY, REF. 1).
Fig. 2. CORROSION FATIGUE CRACK GROWTH RATES UNDER SINUSOIDAL, TRIANGULAR AND SQUARE LOADS. (FROM J. M. HARSON, REF. 1).
Fig. 3 CORROSION FATIGUE CRACK GROWTH RATES AS A FUNCTION OF FREQUENCY OF LOADING. 12Ni-5Cr-3Mo STEEL IN 3% SALT SOLUTION. (FROM J.M. BARSOM, REF. 2).
Selection of materials to resist corrosion fatigue presently rests on a knowledge of laboratory test results for specific materials in specific environments. One should have available the following data, if possible:

1. S-N Curves; \( \frac{da}{dN} \) vs. \( \Delta K \) curves for various environments.
2. Stress corrosion cracking data; \( K_{ISCC} \), \( \frac{da}{dt} \) vs. \( K \) curves.
3. Modified Coffin-Manson data:

\[
\Delta e = C_2 \left[ N_e^{k-1} \right]^{-\beta}
\]

(tabulations of \( C_2 \), \( K \), and \( \beta \) are not generally available at present, but information should accumulate with time).

REFERENCES


DISCUSSION - The author had suggested the existence of a cutoff frequency above which applied loads would not produce crack propagation within usual test duration. Gatts suggested that continuation of testing sufficiently long would lead to eventual crack propagation even at "above cutoff" frequencies. The author acknowledged that this was a controversial area which has received some attention but in which the facts are not fully established for very long time cyclic load application. Hammit's question brought out that the "square" versus "triangular" load-time curves had the following general characteristics:
The effective mechanism through which shot peening improves stress corrosion resistance was identified as the introduction of residual compressive stresses which reduce or eliminate plastic deformation areas due to applied stress. It is well established that sites of plastic deformation, such as slip bands, are preferred sites for environmental attack. Wechsler noted that rubber coatings for ship propeller shafts have been successful in greatly reducing stress corrosion cracking. Although these coatings do not adhere in the presence of a crack, they remain intact and exclude the hostile environment which would otherwise greatly accelerate crack growth rate. To Glaeser’s observation of limited available data on stress corrosion fatigue of high strength and stainless steels, Wei observed that considerable data existed on high strength steels such as 4340, but added that he preferred not to talk about "endurance"; if the presence of a crack is accepted, stress is no longer a descriptive parameter of the crack growth process. Marx was advised that increasing temperature acts to accelerate crack growth rate; as is the general case in all chemical reactions. Gillin reported that tests at the Aeronautical Research Labs in Australia showed stress corrosion cracking to be stopped quite dramatically in certain steels by adding very small amounts of oxygen, apparently contrary to Grosskreutz' report taken from (unspecified) literature. Powell suggested a distinction between "corrosion-induced" fatigue and corrosion fatigue, but the speaker was unable to agree with such distinction. Hammitt suggested that the compressive stresses imposed by cavitation might inhibit effects of stress corrosion fatigue.

5. "GENERAL FRAMEWORK OF UNDERSTANDING STRESS CORROSION CRACKING," by R. Staehle, Professor of Metallurgical Engineering, Ohio State University, Columbus, Ohio 20234.

**Introduction** - This presentation outlines progress in the general understanding of stress corrosion cracking in metals. First, we review some of the early history of stress corrosion cracking and especially that before 1960. Secondly, we review important developments since 1960 in the phenomenological aspects of cracking. Next, we review important contributions to mechanistic understandings of stress corrosion cracking. Finally, we outline some especially useful concepts which are presently available.

Part of the purpose of this presentation is to suggest that very important advances have been made in the understanding of stress corrosion cracking. There are now certain ideas which are sufficiently useful that general predictions can be made. These ideas still lack quantitative substance, but optimistically they furnish a basis for quantitative development.

It is not the purpose of this discussion to consider in great detail all aspects of stress corrosion cracking but merely to highlight important aspects in the categories mentioned above. Detailed discussions of stress corrosion cracking are available, and the most useful and recent are the large volume from the 1967 conference held at the Ohio State University (1), the monograph by Logan (2), and the recent proceedings from the conference in Portugal edited by Scully (3). Previous volumes are available which are also useful and much of the data and suggestions presented therein are still extremely valuable. These include the
first volume published in the AIME-ASTM collaboration (4) in 1944, the volume entitled, physical metallurgy of Stress Corrosion Fracture, published in 1959 (5), and the book edited by Robertson in 1956 (6). No further reference to original sources will be given here as these references are more than adequate to substantiate the discussion herein.

Important Developments Prior to 1960 - Stress corrosion cracking of alloys prior to 1960 was dominated by a number of important ideas. One of the most important of these ideas was that stress corrosion cracking was a "specific ion" proposition, wherein only certain ions caused the cracking of certain alloys. This was, at that time, and still to some extent remains a useful idea although in recent years it has been demonstrated many times that the conditions causing stress corrosion cracking are more general than the "specific ion" idea embraces. On the other hand, the specific ion idea was an extremely useful diagnostic tool and still remains that. This era was dominated by certain other ideas mechanistically. There were a number of the usual suggested mechanisms for stress corrosion cracking including a surface energy argument, a strain induced transformation, film rupture model, and others. None of these were in the least quantitative or predictive.

Important examples of the specific ion concept include the following:

1. The chloride cracking of the stainless steels and aluminum alloys.
2. The ammonia cracking of the copper base alloys.
3. The nitrate and caustic cracking of the low alloy steels.
4. Hydrogen cracking in the high strength steels.

Numerous other examples exist and are well known. However, the cracking to a large extent was dominated by the several mentioned above and most stress corrosion failures could be interpreted thereby. An example of a typical chloride cracking of a stressed stainless steel part is Figure 1 which shows chloride-induced cracking of a stainless steel bellows. The chloride was made available by the expedient of wetting and drying action. This is one of the most common causative processes for chloride cracking of stainless steels. The stress arises from the residual stresses produced during forming the bellows.

These early studies of stress corrosion cracking interpretations were dominated by some relatively straightforward experimental techniques. These involved essentially approaches of the "static fatigue" type which is simply stress vs. time to failure type. Below a certain stress, infinite life was realized. This was effectively the analog of the endurance limit.

Stress Corrosion Cracking Since 1960 - The stress corrosion cracking studies since 1960 have been characterized by a phenomenal increase in the number of mechanistic suggestions for interpreting stress corrosion cracking. Secondly, there has been a major improvement and broadening in the testing approach used in stress corrosion testing. Third, the specific ion concept is all but dead as a generalizable idea, notwithstanding the fact that the specific ion idea is a useful diagnostic tool.

One of the first observations suggesting that specific ions were not responsible for the stress corrosion cracking of alloys was the instance of the high nickel alloy, Inconel 600, undergoing stress corrosion cracking in pure water.
Fig. 1 STRESS CORROSION CRACKING OF STAINLESS STEEL BELLOWS EXPOSED TO CHLORIDE SOLUTIONS. CRACKING CAUSED BY RESIDUAL STRESSES DURING THE COLD FORGING OF THE BELLOWS.
Subsequently, a similar observation was obtained in connection with the stress corrosion cracking of unsensitized stainless steel in connection with the failure of stainless steel fuel elements containing uranium dioxide. These events occurred early in 1960. These events were the harbinger of a rash of cracking phenomena. Probably the most significant cracking phenomenon, which represented a substantial departure from previous history, was the cracking of titanium alloys in N₂O₄. Figure 2 shows an example of a Ti-6Al-4V alloy which failed in the form of a fabricated container. N₂O₄ is not an aqueous environment and it has a relatively high resistivity. It was quite unlikely that this should be an environment in which such virulent stress corrosion cracking could occur. Shortly after the stress corrosion cracking of titanium occurred, the stress corrosion cracking of titanium in methanolic environments was observed. This was again a major surprise in view of the apparent innocuousness of the methanol and the corrosion resistance of titanium. Subsequent to these early observations an extensive number of studies was conducted demonstrating quite clearly that methanol together with small amounts of dissolved chloride and water was a very virulent environment.

With respect to the hydrogen-related cracking of high strength steels it was next found that dry hydrogen, and not hydrogen only in the form of water, but simply dry hydrogen at ambient pressures, was sufficient to cause crack propagation in the high-strength steels.

At the same time that the number of susceptible alloy-environment systems was increasing, an evolution was occurring in the method of testing. Previous to the 1960's most stress corrosion testing was conducted using specimens of smooth surfaces. However, there had always been substantial scattering of results, and, further, it was felt that the most meaningful specimen should contain pre-existing cracks since engineering structures were inevitably in a similar state. The advent of precrack specimens was concomitant with the application of methods of fracture mechanics and the well known parameter of the crack tip stress intensity. Thus the old "applied stress vs. time to failure" was replaced by a stress intensity vs. time to failure. This general approach has proved extremely useful especially in the study of high strength aluminum, titanium, and steel alloys.

Review of Recent Mechanistic Ideas - Since the early 1960's mechanistic aspects of stress corrosion cracking have received vigorous considerations. Probably the first substantial efforts of significance were the general concepts of film rupture developed by Forty and Humble, Westwood and co-workers and Bond and McEvily. This essential idea involves the formation of a brittle layer and subsequent fracture. The propagation of cracks then involves the sequential formation of brittle film and brittle rupture. Another major early idea concerned the process of slip as affected by stacking fault energies. The essential concept here involved those conditions which produced coplanar slip, i.e., low stacking fault energies would favor the onset of stress corrosion cracking and indeed a number of impressive correlations were produced.

Another extremely useful concept which was advocated again by Swann and Nielsen concerning the formation of tunnels which preceded cracking. Thus the propagation of cracking related to the formation of tunnels by corrosion processes and the subsequent tearing of the material. This continues to be an extremely useful concept.
Fig. 2 STRESS CORROSION CRACKING OF Ti-6Al-4V ALLOYS IN N₂O₄. THE TITANIUM BOTTLE IS APPROXIMATELY 18 INCHES LONG AND HAS AN 0.022 INCH THICK WALL. CLOCKWISE FROM YOUR RIGHT: CROSS SECTIONAL PHOTOMICROGRAPH SHOWING TRANSGRANULAR CRACKING FRACTOGRAPH OF SCC REGION, MACRO VIEW OF CROSS SECTION, PLAN VIEW OF INNER SURFACE.
Fig. 3 SCHEMATIC ILLUSTRATION OF SPECIFIC CASES FOR SLIP DISSOLUTION. THE i-t (CURRENT TIME) TRANSIT IS RELATED TO THE RESULTING DISSOLUTION MORPHOLOGY,
Another important mechanistic idea has involved the absorption of environmental species. This idea, articulated by Uhlig, relates to the lowering of metal-metal bond energies by the environment and thereby increasing the capacity for cracks to propagate. Finally, another very powerful idea has been a refinement of the film rupture idea involving the breaking of protective films and their reformation. There are three separate cases for this process. First, if a film is broken and reforms immediately, no material is dissolved and no crack propagates. On the other hand, if the film is broken and a large amount of dissolution occurs, then pitting ensues. Only in the intermediate circumstance when there is sufficient but not too much dissolution is the crack-like morphology observed. Figure 3 illustrates the dissolution morphologies and the current time transients associated therewith. The slip-dissolution idea relates essentially to the lower strength alloys, but depending on the alloy system may relate also to high strength alloys.

A final and important mechanistic hypothesis relates to the effect of hydrogen on the propagation of cracks. It has been a long accepted conclusion from early work by Troiano and others that the high strength steels propagate cracks according to some mechanism involving the absorption of hydrogen and a form of decohesion which results. This idea continues to be an important concept in interpreting the stress corrosion cracking of the high strength steels. More recently this hydrogen-related idea has been applied to the lower strength stainless steels, carbon steels, and aluminum alloys by Troiano and co-workers. At the present time there is a major controversy concerning the applicability of this concept.

REFERENCES


4. Stress Corrosion Cracking of Metals, ASTM-AIME, 1945


DISCUSSION - Staehle agreed that it was not safe to generalize that susceptibility to SCC is low if one is in the "passive" area of the stability diagram. The primary determinant of resistance to SCC is the rate at which the surface film reforms after rupture, and in some passive regions that rate is slow. A
question about the role of alcohol in the cracking of titanium led to recognition of two schools of thought, both of which are actively acquiring data so that a choice at this time would be presumptuous. The electrochemists think it controls the formation of a stable oxide; others consider it as a ready source of hydrogen. Lastly, the role of pH at the crack tip in crack propagation was questioned by Parrish. Staehle felt that it was not clear: the entry rate of hydrogen into the material is the critical factor, and that entry does not require a low pH, but depends upon solution chemistry of the environment and upon alloy chemistry. The pH does, however, give a clue to the relative stability of films—both film thickness and reformation rates have been identified as functions of pH.

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7. "EFFECTS OF TEMPERATURE AND ENVIRONMENT ON SUBCRITICAL CRACK GROWTH," by R.P. Wei, Department of Mechanical Engineering and Mechanics, Lehigh University, Bethlehem, Pennsylvania 18015.

The integrity and service lives of engineering structures are governed by the fracture toughness and the subcritical crack growth resistance of the component materials. While the strength of the structure is governed principally by fracture toughness, its durability is determined primarily by the subcritical crack growth resistance. Subcritical crack growth can occur under both sustained and cyclically varying loads, and can be influenced strongly by temperature and by chemically aggressive environments. Proper understanding of the mechanisms for subcritical crack growth resistance is essential to the development of viable programs for fracture control.

Fracture mechanics based on linear elasticity has emerged as a most useful framework for quantitative studies of subcritical crack growth and fracture in engineering materials. The mechanical crack driving force is unambiguously characterized by the crack-tip stress intensity factor K or stress intensity range ΔK. Currently two different approaches are used, within the general framework of fracture mechanics, for studying subcritical crack growth: the threshold-life approach and the kinetics approach. Schematic representation of data developed by the two approaches are shown in Figure 1 for the case of sustained load crack growth. (Analogous data would be obtained in the case of fatigue.) Because kinetic information is of greater fundamental value, and because life data can be obtained from the crack growth kinetics by direct integration (at least in principle), the kinetics approach is currently more in vogue and is favored.

Subcritical crack growth can be broadly grouped into four categories according to the type of loading and the external chemical environment (1):

1. Sustained load crack growth in inert environments (such as vacuum, inert gases, etc.).
2. Fatigue crack growth in inert environments.
3. Sustained load crack growth in aggressive environments, or stress corrosion cracking.
4. Fatigue crack growth in aggressive environments, or corrosion fatigue.
Fig. 1 SCHEMATIC REPRESENTATION OF THE CRACK GROWTH KINETICS AND TIME-TO-FAILURE UNDER SUSTAINED LOADS
The first two of these are purely mechanical in nature, while the latter two entail mechanical and environmental interactions. All four categories of crack growth are affected by temperature, reflecting the temperature dependence of the kinetics of chemical and deformation processes that control crack growth. Because thermal and chemical variables are inevitably present during service, these factors have received and are being given a great deal of attention.

Subcritical crack growth under sustained loading exhibit typically three stages of growth: Stages I, II and III, Figure 1. Only the steady-state rates of crack growth are depicted in Figure 1. Steady-state crack growth condition is attained when the rate of crack growth becomes independent of time under conditions of constant $K_I$ and constant environment, Figure 2. It is contrasted with the time-dependent nonsteady-state crack growth (transient growth, "incubation", and crack acceleration) under constant $K_I$, Figure 2. Stages I and III depend strongly on the mechanical crack driving force of $K_I$. Stage II crack growth is nearly independent of $K_I$, and is presumed to be rate-limited by the controlling chemical process(es). Useful mechanistic information can be developed from studies of the temperature dependence for Stage II crack growth, and companion surface and electrochemical studies (2-7). Stage I crack growth has a dominant influence on the service lives of structural components and is of primary engineering interest. Studies in this region are difficult because of the practical problems of measuring very slow rates of growth and of the influences of nonsteady-state crack growth. It is hoped that mechanistic studies can lead to the development of procedures for making reliable estimates of the very low rates of Stage I crack growth of engineering interest. A concerted effort in this direction is needed.

Fatigue crack growth is much more complicated. In addition to the metallurgical, environmental and geometrical variables, crack growth is affected by a broad range of loading variables, some of which can interact with the environment. Many of the observed effects of loading variables can be traced directly to environmental interactions (8,9). Typical crack growth kinetics for various alloy-environment systems may be broadly grouped into three types (Figure 3) and have been discussed in detail by McEvily and Wei (9) in relation to the apparent threshold stress intensity factor for stress corrosion cracking, $K_{isc}$.

Type A behavior is typified by the aluminum-water system. Environmental effects result from the synergistic interaction of fatigue and environmental attack. Type B behavior is represented by the steel-hydrogen system where environmental crack growth is directly relatable to sustained load crack growth with little or no synergistic interaction. Type C represents behavior of most alloy-environment systems. Above $K_{isc}$, the behavior approaches that of Type B, whereas, below $K_{isc}$, the behavior tends toward Type A with the associated interaction effects. For Type B and Type C (above $K_{isc}$), the effects of loading variables (frequency, waveform, etc.) may be directly related to the contribution from sustained-load crack growth. Crack growth response to frequency and waveform on Type C systems below $K_{isc}$ and in Type A systems cannot be explained simply at this time.

Environmental effect for certain steels was observed to be a maximum for a
Fig. 2 SUSTAINED-LOAD CRACK GROWTH UNDER CONSTANT $K_I$ SHOWING INCUBATION, CRACK ACCELERATION AND STEADY-STATE STAGES OF CRACK GROWTH.

AISI 4340 STEEL - TEMPERED AT 400°F (204.5°C)  
DISTILLED WATER AT ROOM TEMPERATURE

$K_I = 27$ ksi $\sqrt{\text{inch}}$

$K_I = 19$ ksi $\sqrt{\text{inch}}$

CRACK GROWTH RATE, $\frac{d\alpha}{dt}$, $10^{-3}$ inch/minute

ELAPSED TIME, minutes
Fig. 3 TYPES OF FATIGUE CRACK GROWTH BEHAVIOR
specific frequency and approached zero at higher and lower frequencies (10,11), and was found to be dependent on the waveform. Environmental effect was large for waveforms with "slow" rise-time (such as sine and triangle) and was quite small for those with "high" rise-time (such as square-wave) (10). The waveform effects were not observed in aluminum-water systems (12). The results indicate that these effects are intimately related to the reaction kinetics at the crack tip and need further investigation. Similar to sustained load crack growth, fatigue crack growth studies may be confounded by a range of nonsteady-state phenomena (13). These nonsteady-state phenomena require further attention.

The effects of load interactions in variable-amplitude loading are very complex and can be very large (14). Delay in fatigue crack growth produced by load interaction can be affected by a broad range of loading variables, and by temperature and service environments. These effects are significant to design and fracture control and need to be fully explored.

Ideally, it is desirable to characterize the subcritical crack growth behavior in terms of all of the pertinent variables

\[ \frac{da}{dt} = F(K, T, \ldots) \]

and

\[ \frac{\Delta a}{\Delta N} = F_2(\Delta K, \beta, T, R, \ldots). \]

Obviously, such a complete characterization is not feasible and cannot be justified. Data, therefore, must be obtained under certain restricted conditions consistent with the intended service applications. Having obtained the requisite data, one can integrate the rate equations, in principle, to determine the service life or to specify an appropriate inspection interval. The lower limit of integration is usually defined on the basis of nondestructive inspection (NDI) capabilities; the upper limit being defined by either fracture toughness or a predetermined allowable crack size consistent with inspection requirements. The application of kinetic data to design must, in addition, take full account of the effects of nonsteady-state crack growth and of load interaction. Careful consideration must be given to these factors in the development of a viable fracture control program.

REFERENCES


**DISCUSSION** - Wei indicated that tests to determine the effect of the waveform of applied load had been run in the absence of a corrosive environment, and that there had been found to be no effect. Wiederhorn asked the reason for a discontinuity which Wei had reported in the shape of a crack length vs. time curve, the discontinuity occurring at the point where the test was stopped overnight. Wei indicated that two factors were probably responsible: (1) some relaxation takes place when the specimen is left unloaded, and (2) some time is probably required to establish an equilibrium concentration level of whatever the embrittling species is at the crack tip.

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Interaction of an active solvent environment with a polymeric solid can produce a variety of adverse physical changes such as uniform softening and ultimate dissolution of uncrosslinked systems; inhomogeneous swelling or plasticization leading to large local deformations and/or stresses; chain scission and degradation of molecular weight; uniform swelling and permeation of crosslinked elastomers, or inhomogeneous swelling and interfacial failure of filled elastomers. One or several of these factors can contribute to observable reductions in
modulus, softening point, fracture strength, impact strength, optical clarity, permeability, fatigue life and so on. In this talk, two specific problems are considered: (1) inhomogeneous swelling in filled elastomers and the characterization of polymer-solvent interactions by swelling pressure techniques; (2) stress field criteria for crazing and yielding in glassy polymers and preliminary effects of solvent environments.

1. Inhomogeneous Swelling - Hard filler particles are used to enhance toughness, strength, and abrasion resistance of elastomeric materials. The filled elastomer is a composite of unusual properties in that the matrix is finitely deformable. This leads to considerable complexity when the swelling method is used to characterize the crosslink density of the filled material. An exact solution for the inhomogeneous swelling, stress, and deformation fields about an isolated hard filler particle embedded in and bonded to a swollen elastomeric matrix has been obtained recently (1). Experimental verification has been obtained using birefringence techniques (2). Thus, we are now able to predict interfacial stresses and deformations in filled elastomers as a function of crosslink density, solvent strength and filler modulus and to relate such information to filler-matrix bonding failure.

In many filled elastomers, the interfacial bonding may be of secondary (van der Waals) rather than primary (covalent) origin. This leads to what may be described loosely as a boundary layer of immobilized elastomer surrounding each filler particle. Knowledge and characterization of this filler-matrix interaction is vital to the understanding of the filler reinforcement mechanism. It is difficult to use swelling techniques to characterize this effect since, as we have just shown, interfacial failure is very likely to occur. In order to circumvent the filler-matrix separation, we have developed a new technique whereby the filled elastomer is constrained to constant volume while solvent is allowed to diffuse into the sample. The solvent absorption rate and stress generation rate are measured, the transient behavior giving diffusion constants and the equilibrium "swelling pressure" (for no volume change) giving a measure of the polymer-solvent interactions. The latter quantity is independent of crosslink density (since there is no conformational entropy change for the rubber network), but is dependent on the thermodynamic state of the elastomer. In this way, we hope to investigate the role of interfacial immobilization of rubber in the filled elastomer.

2. Stress Field Criteria for Yielding and Crazing - Multiaxial studies have been performed on amorphous glassy high polymers and indicate that two distinct stress field criteria exist, one for normal stress yielding (or crazing) and one for shear yielding (3,4). Both criteria depend on the isotropic as well as deviatoric component of the stress tensor. The two yield criteria correctly predict the effects of stress field on the observed yield behavior; for example, a hydrostatic pressure induced brittle to ductile transition, and a variety of yield behaviors in the second quadrant of stress space. Preliminary studies indicate that the crazing criterion also applies to solvent-induced craze formation. Craze propagation studies indicate that growth rates are affected by stress level in the same way as fracture strengths.
REFERENCES


DISCUSSION - The material used in the reported tests of a filled elastomer was natural rubber, which is transparent. The filler consisted of glass spheres. It was reported that Professor Richard S. Stein at the University of Massachusetts had made independent determinations using light scattering intensity measurements. The deformation fields reported by the speaker were closely confirmed.

8A. This concluded the second technical session. Following a luncheon recess, A.J. Koury of the Naval Air Systems Command chaired the third technical session. Mr. Koury opened the session with a brief description of the Navy's Analytical Rework Program, comprised of engineering analyses performed to the extent necessary to determine the current overall structural integrity and material condition of an aircraft or its components.


Powder coating technology has provided a means of applying resin coatings to substrates via processing techniques which have two distinct advantages over conventional coating procedures. The first and probably most significant advantage from an ecological standpoint is the elimination of solvent carriers. The absence of solvents eliminates the emission of fumes and vapors thereby providing an environment that is virtually free of pollutants. Safety standards are also improved because the hazard of fire is substantially reduced. The second advantage that results from this processing technology is the ability to form protective resin coatings which could not be applied by any other technique without difficulty, because of the poor solubility of the particular resin in most solvents. Thus various coating properties can be obtained which were not previously available.
The commercially available powders that are used include both thermoplastic (polyamides, polyvinyl chloride, fluorocarbons, chlorinated polyethers, polyolefins, cellulosics, acrylics) and thermosetting (epoxies, polyesters) resins. The choice of a resin for a given application is dependent upon the specific creating properties desired.

This talk reports on the effectiveness of polymer coating materials in alleviating a particular materials problem. The specific areas investigated were: (1) spline assemblies (fretting wear); (2) aircraft leading edge attack (erosion and abrasion); (3) metal fatigue (anti-fatigue coating); and (4) magnesium alloys (corrosion prevention).

Two convenient methods are available for deposition of powder coatings, viz. fluidized bed and electrostatic spraying. Fluidized-bed coating requires heating the substrate above the fusion temperature of the powder and then dipping it into a bed of "finely divided", dry fluidized powder which melts and fuses on the heated surface to form a continuous film. The term "fluidized" describes the fluid-like nature of the resulting powder/air mixture, the air causing the particles to be in continuous motion.

The electrostatic spray technique (apparatus shown in Figure 1) requires electrically grounding the substrate to be coated and then spraying it with charged powder particles. This is accomplished by contact on passing the coating particles through a suitably shaped electrode (see Figure 2). The charge is transferred to the powder particles, and they are electrostatically attracted to the grounded substrate at room temperature. The charged particles will cling to the substrate until the charge is dissipated. This allows ample time to fuse the powder layer into a continuous film. The major difference between the two techniques is that in the fluid-bed process the substrate must be preheated to 100-150°F above the melting point of the powder, whereas in the electrostatic spray process the temperature exposure is essentially the fusion point of the powder. This difference is important when certain aluminum or magnesium alloys are to be coated, since the mechanical properties of these alloys may be seriously degraded by exposure to an elevated processing temperature.

Substrate Materials - In the electrostatic spray process, the powder-coated substrate is subjected to a heating operation in order to fuse the powder particles into a continuous film. For Nylon 11 material the fusion point is 367°F; therefore it is only necessary to heat the powder-coated substrate to this temperature. For given substrate dimensions, the time required to effect fusion will vary with temperature as shown in Table I.

When subjecting aluminum or magnesium alloys to the electrostatic processing, the heating operation may cause detrimental effects to the mechanical properties, e.g., a decrease in ultimate tensile strength and a decrease in tensile yield strength. Table II shows the percent change in these properties from the room temperature values for various aluminum and magnesium alloys which were subjected to 400°F for 1/2 hours. Although this table is not exhaustive and only covers alloys for which data is available, it is evident that changes in these properties are effected by a heating operation at 400°F. In selecting an aluminum or magnesium alloy for this processing technique, the effect of thermal conditions on mechanical properties must be considered.
### TABLE I

FUSION TIMES AT VARIOUS TEMPERATURES FOR A NYLON 11 COATING ON 4130 STEEL (SUBSTRATE DIMENSIONS 3" x 6" x 1/32"")

<table>
<thead>
<tr>
<th>OVEN TEMPERATURE °F</th>
<th>FUSION TIME, MIN.</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4</td>
</tr>
<tr>
<td>450</td>
<td>2</td>
</tr>
<tr>
<td>500</td>
<td>1</td>
</tr>
</tbody>
</table>

### TABLE II

PERCENT DECREASE IN ULTIMATE TENSILE STRENGTH AND TENSILE YIELD STRENGTH FROM ROOM TEMPERATURE VALUES FOR VARIOUS ALUMINUM AND MAGNESIUM ALLOYS AFTER EXPOSURE TO 400°F FOR 1/2 HOUR

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>ULTIMATE TENSILE STRENGTH</th>
<th>TENSILE YIELD STRENGTH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aluminum</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014-T6</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>2024-T3</td>
<td>6</td>
<td>13</td>
</tr>
<tr>
<td>2024-T4</td>
<td>6</td>
<td>13</td>
</tr>
<tr>
<td>2024-T6</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>2024-T81</td>
<td>0</td>
<td>.5</td>
</tr>
<tr>
<td>2024-T86</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>5052-H34</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>5052-H38</td>
<td>0</td>
<td>.5</td>
</tr>
<tr>
<td>6061-T6</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>7079-T6</td>
<td>10</td>
<td>18</td>
</tr>
<tr>
<td><strong>Magnesium</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZ92A-T6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>EZ33A-T5</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>HK31A-H24</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HK31A-T6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HZ32A-T5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HM21A-T8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HM31A-T5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Salt Water Corrosion Test - One test used to evaluate the corrosion resistant properties of plastic coatings is the sulfurous acid/salt spray test detailed in Ref. (2). Coated discs are placed in specimen holders designed so that the coated surface of the specimen is exposed to the corrosive environment. The specimen holder consists essentially of a glass cylinder fitted with a plastic screw cap with center removed. Aluminum water jackets are filled with \( \text{EC} \)-water and placed in the specimen holders to contact the coated discs and allow a fine condensate to form on the surface of the disc. A combination of 2 hours spraying and 2 hours drying time constitute a test cycle. Table III shows the results of this corrosion test on uncoated alloys, nylon coated alloys and other metal treatment processes. After 28 cycles the test was terminated and the nylon coating was removed from the discs as described earlier (see Figure 3). No evidence of corrosion was observed. In contrast, AZ31B discs coated with DOW 17 showed evidence of pitting after 10 cycles, and a chromated AZ31B specimen exhibited failure after only 1 cycle. The uncoated specimens also failed in 1 cycle of testing.

**TABLE III**

SYNTHETIC SEA-WATER SULFURIC ACID CORROSION TEST RESULTS

<table>
<thead>
<tr>
<th>ALLOY DESIGNATION</th>
<th>COATING</th>
<th>CYCLES TO FAILURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 1020 Steel</td>
<td>Bare</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>AISI 1020 Steel</td>
<td>Nylon 11</td>
<td>28+</td>
</tr>
<tr>
<td>AZ31B Mg</td>
<td>Bare</td>
<td>1</td>
</tr>
<tr>
<td>AZ31B Mg</td>
<td>Nylon 11</td>
<td>28+</td>
</tr>
<tr>
<td>AZ31B Mg</td>
<td>Chromated</td>
<td>1</td>
</tr>
<tr>
<td>AZ31B Mg</td>
<td>Chromated +</td>
<td>28+</td>
</tr>
<tr>
<td>AZ31B Mg</td>
<td>DOW 17</td>
<td>10</td>
</tr>
<tr>
<td>AZ31B Mg</td>
<td>DOW 17 +</td>
<td>28+</td>
</tr>
<tr>
<td></td>
<td>Nylon 11</td>
<td></td>
</tr>
</tbody>
</table>

Abrosion Test - The S.S. White abrasion test apparatus was employed to study the abrasion resistance properties of Nylon 11 coatings. After fusion of the nylon coating, two techniques are available for cooling the specimen to room temperature. The first is to allow the heated specimen to cool slowly at room temperature while the second involves a quenching operation using water. It is considered that the slow cool operation produces a nylon coating with a significant crystalline phase while the fast cooling operation produces a larger amorphous phase. Table IV shows the difference in abrasion resistance characteristics for Nylon 11 coatings based on quenching techniques. Results using an aliphatic polyurethane coating (Laminar X 500), which is commonly used on aircraft leading edge
applications, are included for comparison purposes. The test specimen is located at a fixed distance from a spray nozzle. The abrasive material (50 μm Dolemite) is forced through the spray nozzle at a given pressure, and the time required to completely abrade the coating is recorded. It is evident from Table IV that the nylon coating with the crystalline phase (air quench) is more abrasion resistant than the water quench (amorphous phase) coating. However, both coatings are superior to the polyurethane coating with respect to abrasion resistance.

TABLE IV
S.S. WHITE ABRASION TEST RESULTS

<table>
<thead>
<tr>
<th>Abrasive: 50μ Dolemite (S.S. White #2 abrasive)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEST SAMPLE</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>Nylon 11 (Air Quench)</td>
</tr>
<tr>
<td>Nylon 11 (Water Quench)</td>
</tr>
<tr>
<td>Polyurethane</td>
</tr>
<tr>
<td>Polyurethane</td>
</tr>
</tbody>
</table>

Spline Wear Test - Antiwear properties of the materials have been examined using the Southwest Research Institute spline wear test apparatus, Ref.(3). An MoS₂ diester grease is applied to the teeth of the external spline coated with the Nylon 11. The internal spline is also packed with grease and fitted to the external spline. The internal spline is clamped in a fixed position and the flanged end of the external spline is caused to gyrate, thereby simulating the oscillatory motion of a pair of angularly misaligned splines. A load of 25 pounds is applied to the torque rod producing a tooth contact pressure of 3500 psi. The gyrationary motion is produced by placing a nonrotating gyrator shaft eccentrically within a cylindrical drive shaft which rotates at 4400 rpm. Misalignment is .006 inch/inch of spline length. The test is run at 250°F with heat provided from heating coils placed in the asbestos covered oven that surrounds the test specimen. The test is instrumented to monitor specimen temperature, wear rate and support bearing temperature. Wear of the spline is measured by movement of the lever arm and the changing position of the lever arm is continuously recorded. Results of the laboratory tests show that a lubricated spline without a Nylon 11 runs for 40 hours. A spline treated with the Nylon 11 and the same grease ran for 160 hours under the same test conditions.
1. Mg ALLOY — NO PROTECTIVE COATING
2. Mg ALLOY — CONVENTIONAL COATING
3. Mg ALLOY — NYLON II COATING
4. Mg ALLOY — NYLON II COATING REMOVED

SULFUROUS ACID SALT SPRAY CORROSION

Fig. 3 SULFUROUS ACID SALT SPRAY CORROSION
Fatigue Life Tests - The Tatnall-Krouse constant speed flexure fatigue apparatus was used to evaluate the fatigue properties of Nylon 11 coated steel and titanium alloy specimens. Flexure fatigue specimens with a thickness of .035" for AISI 1010 steel and .076" Ti-6Al-4V alloy were coated with Nylon 11. Table V shows the average number of cycles to fatigue failure for the various test specimens studied. It is evident that the use of a Nylon 11 coating on the steel or titanium alloy substrates significantly increases the fatigue life compared to noncoated specimens.

**Table V**

**FATIGUE TEST RESULTS**

*(Tatnall-Krouse Constant Speed Flexure Fatigue Apparatus)*

<table>
<thead>
<tr>
<th>SPECIMEN</th>
<th>COATING</th>
<th>THICKNESS (MILS)</th>
<th>LOAD (KSI)</th>
<th>AVERAGE CYCLES TO FAILURE ($10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 1010 Steel</td>
<td>None</td>
<td>-</td>
<td>40</td>
<td>200</td>
</tr>
<tr>
<td>AISI 1010 Steel</td>
<td>Proprietary Primer</td>
<td>0.5</td>
<td>40</td>
<td>220</td>
</tr>
<tr>
<td>AISI 1010 Steel</td>
<td>Nylon 11 Primer</td>
<td>7.5</td>
<td>40</td>
<td>496</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>None</td>
<td>-</td>
<td>80</td>
<td>75</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>Proprietary Primer</td>
<td>0.5</td>
<td>80</td>
<td>115</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>Nylon 11 Primer</td>
<td>7.0</td>
<td>80</td>
<td>1000⁺</td>
</tr>
</tbody>
</table>

⁺ Indicates test discontinued; no failure observed.

**Thermal Stability** - Samples of Nylon 11 coated steel and aluminum panels were subjected to temperatures in the range of 300°-400°F for periods up to 24 hours. The nylon coated panels subjected to 400°F became very tacky after 4 minutes exposure due to the resin melting; however, after exposure for 4 1/2 hours the coating darkened, indicating decomposition. On cooling down to room temperature the coating was still intact, suffering no loss of adhesion. The panels at 300°F and 350°F for 24 hours darkened to a lesser extent, again showing no loss of adhesion. However, it is recommended that the coating not be subjected to temperatures greater than 280°F for extended periods.
Nylon 11 Overcoat on Polyurethane - Nylon 11 can be used to overcoat polyurethane finishes, provided the polyurethane substrate is first primed with the proprietary primer. However, no performance tests have been performed on this coating.

Fluid Resistance - Fluid resistance data was obtained for Nylon 11 coated aluminum panels according to the method outlined in reference (4). Compatibility of the Nylon 11 coating with the following fluids was studied:

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-L-5606 Hydraulic Fluid, Petroleum Base; Aircraft, Missile and Ordnance</td>
<td>2. MIL-C-81309A Corrosion Preventive Compound, Water Displacing, Ultra-Thin Film.</td>
</tr>
<tr>
<td>MIL-L-23699 Lubricating Oil, Aircraft Turbine Engine, Synthetic Base</td>
<td>DISCUSSION - Jackson suggested that baked-on metallic lubricants might be good for the spline application mentioned by the speakers. Devine noted that these had been tested, but were not competitive in the present context where a combination of wear and corrosion resistance was sought. The baked-on molys, for example, could withstand a maximum of four corrosion cycles while nylon was going strong after 28. Jackson noted further that manufacturers of chemical and abrasive fluid pumps were using polyurethane as a total coating, with success, and Koury confirmed that his material was in extensive use in the Navy as a universal coating. To Snediker, it was indicated that coating thickness was controlled in the electrostatic process by spray time, powder flow rate, and particle size used.</td>
</tr>
<tr>
<td>MIL-A-8243 Anti-icing Fluid</td>
<td></td>
</tr>
<tr>
<td>TT-S-735, Type II Standard Test Fluids, Hydrocarbon</td>
<td></td>
</tr>
</tbody>
</table>

Two coated panels were immersed in each of the above fluids for 24 hours after which each panel was rinsed in aliphatic naphtha and dried. The panels were then examined for any evidence of softening, lifting, blistering, cracking or peeling. Two parallel scratches, 1 inch apart, were then made on the panel utilizing a stylus. A piece of masking tape placed perpendicular to the scratches was then pressed to the panel. Removal of the tape with an abrupt motion will show any evidence of film removal. None of the panels tested in the above manner showed any evidence of incompatibility with the fluids tested.

REFERENCES

2. MIL-C-81309A Corrosion Preventive Compound, Water Displacing, Ultra-Thin Film.
all combined by operator judgement. Stern questioned how fitting tolerance was maintained in a coated spline; the procedure used was to undercut the spline by about 6 mils and apply a coating of like thickness. The same lubricant was used for coated and uncoated splines obtained in the contact areas of interest; some irregularity was found at tooth ends, but it was unimportant. Jackson suggested use of tungsten carbide applied with a detonation gun to splines to produce superior coatings less than 6 mils thick; Devine and Koury acknowledged that there were specialized coatings which were superior for particular limited applications, but stressed that their object was a multi-purpose substance and process whose use could be standardized as much as possible; nylon seemed to approach this ideal most closely. Heaviest items to be coated for service to date were indicated to be aircraft landing wheels.

10. "ENVIRONMENTALLY INDUCED FAILURES IN THE LUBRICATION OF MARINE MACHINERY," by Nathan Glassman, Naval Ship Research and Development Center, Annapolis Laboratory, Annapolis, Maryland 21402 (Secretary's summary)

The recognition and discussion of failures in terms of "environmental effects" has not typically been the case in the past in the area of marine lubrication. This may well be the result of a generalization that machinery systems are internal systems, thus shielded or able to be shielded from the rigors of the external environment. Unfortunately, the external environment of seawater and salt air can find its way into machinery systems; machinery systems can create their own internal corrosion environment, and man by his choices of machine design can create an internal machinery environment that can materially affect the reliability and maintenance of machinery systems. It is the latter, man-made, internal machinery system environment that requires the greatest attention in the prevention of mechanical failures.

Some Notes on the Marine Machinery Environment - In their appeal for standards in ocean technology, Bloomquist et al. (1) refer to the ocean environment as a unique and complex variable that must be considered in standardization of procedures for the evaluation of materials and components. In connection with defining the marine machinery environment, outstanding service is performed by the Society of Automotive Engineers' Hydrospace Information Report AIR 1063, "General Environmental Requirements for Deep Submersible Vehicles and Submarines" of 15 April 1969 (2). The deep submergence fluid technologists (3, 4) recognize that lubricants and fluids provide the functions of: lubrication, power transmission, and environmental control. Often the success or failure of a machinery system is tied to the ability to surround it with a fluid environment other than the atmosphere or the sea. A host of liquids ranging from kerosene up to oils of approximately SAE 20 viscosity, ranging from hydrocarbons to esters, to silicones, etc. have been used as encapsulating environmental fluids (3, 4). Information such as fluid behavior when seawater intrudes into this environment, when pressure increases, when solids are produced by electric arcing is needed in advance if reliable system performance is to be assured.

Turning now to surface or near surface lubricated machinery systems, what is the picture of the environment therein?
King and Glassman (5) reviewed Navy MS 2190TEP turbine lubricating oil experience. In addition to noting that a variety of different formulations were able to meet the same oil specification requirements, they also provided information on the conditions prevailing in a number of machinery systems lubricated by this oil, and on the effects of use on the oil's stability. At that time 25 different additive compounds were being used and the base lubricant into which these additives (in different combinations and amounts) were being added was not a single material but varied from supplier to supplier. This was possible since the oils were procured under a specification defining performance as measured by a series of tests considered significant and not by restrictive definitions of compositions to be used. Ten instances related to oil performance complaints were examined. Of these, five dealt with the observation of sludging and deposits, two with the observation of rust and two with equipment damage. Contamination ranked high as a cause leading to questions of oil or system performance: sand and water, seawater, rust preventive or oil additive residues. In the two instances where equipment damage was involved (wiping of all main turbine engine bearings), externally generated contamination in the form of sand and seawater and internally generated contamination in the form of loose galvanized metal were indicated as the cause of the failures.

MacDonald (6) associated steam turbine operating problems such as gear scuffing polished bearings, sluggish governor operation and bearing "machining"-type failures with solids in the lubricating oil. He postulated the internal turbine system as saturated with moist air, having free water in the oil and on system metal surfaces ranging from a trace to a large amount. He noted the pH of the water might vary from acid to alkaline. Water was seen as a source of system solid deposits (rust from ferrous metal surfaces in both the liquid and vapor spaces). Rust poses several threats to machinery life. He also noted that air was present in large quantities as a contaminant in turbine oils and that its release contributed to ferrous metal rusting; he speculated that nonferrous metal (copper, zinc) deposits are formed by reactions of oil additives with system metals under the accelerating influence of water. King and Glassman (7) showed that some copper alloys (70/30, 90/10, and Admiralty Metal) could react with seawater or distilled water in a 21-day immersion test at 140°F in the presence or absence of oils. In fact, the oils procured under the same specification but of different formulations showed varying degrees of inhibition or acceleration of the amount of solid reaction products formed depending on which alloy was used. They also described the marine hydraulic system seawater entry problem, noting that perhaps no other class of marine machinery showed as much evidence of apparent failure to recognize the existence of the marine environment. Seawater in a hydraulic system can cause damage by direct corrosion of metal surfaces, altering lubricant viscosity (up or down) to create wear, generating solid products (corrosion) which cause malfunction in close tolerance actuating mechanisms.

Much can be done to reduce the role of solids in contributing to failures. This is by collecting, codifying, and disseminating the best practices known at any point in time for lubricating oil system design, preparation, oil selection, purification procedures and inspection, and maintenance procedures. Such an effort has been underway for many years under the auspices of the ASTM-ASME-NEMA Joint Committee on Oil Systems Turbines. The output takes the form of various ASTM-ASME Recommended Practices with ASME Standard Numbers:
STANDARD | TITLE OF RECOMMENDED PRACTICE
--- | ---
ASME 115D | Design of Lubricating Systems for Marine Steam Turbine Pumps for Various Ship Services
ASME 119 | Flushing and Cleaning of Marine Auxiliary Machinery Lubricating Systems
ASME 121 | Purification of Lubricating Oil in Marine Steam Turbine Driven Auxiliary Machinery
ASME LOS 2Cl | Flushing and Cleaning of Lubricating Systems of Various Turbine Driven Pumps for Marine Service
ASME LOS 4Cl | Flushing and Cleaning of Gas Turbine Generator Lubricating Oil Systems

This discussion of the environment has been relatively qualitative and on a macroscale. Studies of the world that exists on the surfaces of metals and the interaction of those surfaces with the liquid lubricant were described in great detail at the recent NASA Symposium (January 1972) on an Interdisciplinary Approach to Liquid Lubricant Technology. In describing the chemical and physical nature of lubricants, the nature of solid surfaces, the current estimates of the roles of adsorption, wear, corrosion, erosion and thermodynamics in lubrication, that symposium serves the useful purpose of this meeting in insuring against oversimplification of the nature of the machinery environment (8 - 14). In the case of the marine machinery environment, the complexity at the critical machinery surfaces is increased by the entry of the external marine environment into the lubrication system.

Some Illustrations of Approaches to the Marine Machinery Environment Threat:

The Machining-Type Bearing Failure Problem - During the early 1960's an unusual and severe type of bearing failure occurred in a number of marine steam turbines. This was typified by "machining" of the harder journal and/or thrust collar materials. From the outward appearance of the damage, they have also been called "wire-wool" failures. Another characteristic is the appearance of built-up hard scabs on the softer bearing metal.

A mechanism for the initiation and propagation of a machining-type failure was postulated. This assumed the entrapment in the bearing of an initially hard, sharp particle(s) which is susceptible to becoming harder than the rotating steel shaft or collar and the partial embedment of this particle(s) in the softer babbitt metal. The particles then act as cutting tools which perform a lathe turning operation. The detailed processes whereby the initiating particles are hardened, produce primary slivers which then abrade the harder bearing member and are built up by adhesion are described in detail by Karpe (15). In a laboratory bench test, machining-type failures were induced with those oils and steel thrust collars with a known service history of having been involved in a machining-type failure.
With respect to the lubrication environment, the test results showed that high-chromium alloy steels lubricated with oils without chlorine-containing additives are vulnerable to machining failures. They also showed that low chromium-containing steels (less than 2%) have their failure propensity enhanced when using lubricating oils containing chlorine-containing additives. As a result of this work, the use of chlorine-containing load-carrying additives in the steam turbine oil was prohibited. The use of high chromium steels (4 plus per cent) also was eliminated. New emphasis was placed on developing better system cleaning procedures, such as finer full-flow particulate solid contaminant particles removal filters. This problem has disappeared. Further information of the test procedure can be obtained from Karpe's work (15, 16).

The Rolling Contact Fatigue Problem - For some years we have been studying the role that water plays in the rolling contact fatigue process. The seed for this interest was the work of Grunberg and Scott (17) who in 1958 reported that water in the lubricant reduces surface fatigue life in rolling-contact lubrication. Schatzberg and Felsen (18), using a four-ball machine modified to simulate an angular contact rolling bearing, showed that as little as 0.01% dissolved water in the lubricant causes a significant reduction (40%) in surface fatigue life. A smaller reduction was obtained when oxygen was present. They proposed a capillary crack condensation hypothesis according to which the water condensed in the surface micro-cracks promotes corrosion and hydrogen embrittlement, which under dynamic stress reduces the time for the crack to grow to critical size and a spall occurs. Schatzberg (19) using the same apparatus and experimental procedure showed that the addition of 0.1% isopropylaminoethanol completely counteracts the detrimental influence of 1% seawater emulsified with the lubricant. He postulated that this was due to the additive's ability to capture hydrogen ions formed within the crack and thereby inhibit hydrogen embrittlement. It was noted that the high stress levels used, 925 to 1300 ksi maximum Hertz compressive stress, might be introducing effects not seen under commonly used bearing loads. Felsen (20) using flood-lubricated actual size 208 angular contact ball bearings at 330 ksi maximum Hertz compressive stress, showed reductions in $B_{10}$ and $B_{50}$ rolling contact fatigue lives from 25 to 80% dependent on lubricant used when 1% by volume of seawater was added. The lubricants used included mineral oils with and without additives. One of these oils was the same emulsifying oil Schatzberg had used for his inhibition experiments. This oil gave $B_{10}$ and $B_{50}$ fatigue life reductions in the presence of 1% seawater of 22.5 and 46% respectively - which are comparable to the 48 and 60% reductions Schatzberg reported for his more highly loaded (1000 ksi maximum Hertz compressive stress) experiment. At this point we are trying to demonstrate the ability of isopropylaminoethanol to inhibit rolling contact fatigue in real ball bearings. To date, we have not been successful. We are looking for reasons why. At present, we are certain that water in the lubricant environment has a deleterious effect on rolling element life and that the nature of the lubricant can have a profound influence on rolling element life. This last is supported by the work of Rounds (21) and Muller as reported by Fein (14).

Influence of the Environment on Sliding Wear - Schatzberg (22) in his study of the influence of oxygen and water in the lubricant on wear used a four-ball wear machine with AISI 52100 steel balls, four lubricants of two different viscosity levels and four different formulations. He noted that depending on the environment (wet or dry, oxygen present or absent), the ability of a lubricant to
minimize wear is affected when the time-dependent experiments are conducted under light loads (non-scuffing regime). Brown (23) studied the effectiveness of marine hydraulic and lubricating fluids in providing reduction in wear of steel-on-bronze surfaces. His work supports the premise that differences in wear can be obtained with lubricants procured under a common specification.

I believe that charting lubricant-machinery component interactions with respect to machinery compatibility or increased machinery protection is a pay-off area for research to reduce failures; that continuing to search for counter-measures to the effects of water entering the lubricant environment is another research pay-off area to reduce failures; that continued efforts by Government agencies, technical and professional societies to codify and communicate the marine environment and machinery practices to be followed therein also are pay-off areas for the prevention of mechanical failures.

REFERENCES


-56-


DISCUSSION - The speaker indicated that the bearing tests which he had conducted were done under load, details of which are given in the references. He has not investigated oil mist lubrication systems.

*****************************************************************************

-57-
While continuing advances in the state-of-the-art have resulted in substantial increases in the average life of rolling-element bearing/lubricant systems, considerable scatter in the life still remains. This is due to inevitable manufacturing variations coupled with damage (or high stress conditions) resulting from installation or environmental effects such as handling, corrosion, vibration, etc. Some means must therefore be employed to identify and screen out those units containing life limiting defects prior to service. In order to realize the long life potential inherent in a given design, Acoustic Signature Analysis (ASA) was developed.

The Acoustic Signature Analysis technique is based on the measurement, analysis and interpretation of internally generated bearing vibrations. It is directed toward the detection of life limiting defects before performance degradation has taken place. The key to the ASA process lies in the interpretation of the observed signature spectrum with the aid of a computer generated predicted spectrum, derived from a mathematical model of the test bearing(s).

In this talk the ASA technique is described along with examples of its application to the detection of subtle bearing defect conditions both inherent in the bearing as manufactured and resulting from installation and/or environment effects. While the emphasis is on gyro bearings, there is a brief discussion of the application of ASA to momentum wheels and component level (bearings by themselves) ASA. The latter tests indicated that many of the acoustically-detected bearing anomalies were induced by the installation.

One study discussed yielded an 82% correlation between ASA techniques and the results of subsequent tear-down analyses. The ranking of defect severity for several life-critical defect modes is discussed as a quantitative means of determining flight worthiness.

Signature Analysis Concept - For several years, we have been developing a nondestructive testing technique based on the measurement and interpretation of internally-generated vibration "signatures". Particular emphasis has been placed on detecting the presence of life-limiting defects in electro-mechanical components before such defects cause detectable performance degradation. Such techniques have been successfully applied to a wide variety of subjects, ranging from jet engines to the human heart.

Figure 1 is a block diagram of the Acoustic Signature Analysis concept. Vibrations generated within the test specimen are detected, recorded, subjected to one or more forms of instrumental analysis, then displayed as a "signature".

A detailed analysis of component geometry, operating speeds, and other factors is also performed. From this analysis, a mathematical model is developed to predict the vibration signature (i.e., frequency/amplitude/time patterns) to be expected for normal conditions, and for the presence of various defects. The measured signature and the predicted signatures are then compared, and from the correlations observed, conclusions are reached with regard to the internal conditions of the test specimen.
Fig. 1. Acoustic Signature Analysis Process.
The above, of course, is the ideal flow, as shown by the solid lines in Figure 1. In actual practice, both the instrumental analyses and math-model development are iterative processes. As more is learned about interpretation of the display signatures, analysis requirements (e.g., sample duration and bandwidth) are modified accordingly. The analytical model is also modified and updated as empirical data becomes available. These "feedback" paths are shown as dotted lines in Figure 1.

One point should be noted in the application of Acoustic Signature Analysis to spacecraft components: this technique is designed to supplement, not augment, more conventional test methods. The value of the signature analysis approach lies in its ability to detect the presence of defect conditions before performance degradation has taken place, and thus, to identify defect conditions not generally detectable by ordinary means. Of special interest to the Space Systems Operation, of course, is the detection of those defect conditions that could limit device life, and thus, prevent completion of extended missions.

Application to Miniature Precision Bearings - Acoustic Signature Analysis data on bearings is obtained by temporarily cementing an accelerometer to the test specimen. (The optimum location, not usually critical, may have to be determined by experiment.) While the specimen is operating normally, the output of the accelerometer is recorded; a few seconds of data is sufficient. A selected portion of the recording is formed into a continuous loop and played back for analysis. While more sophisticated instrumentation is sometimes employed, the principal tool for analysis has been the narrowband recording wave analyzer. This instrument produces an accurate plot of vibration amplitude versus frequency; this is the "signature" used for most analysis.

Mechanical defects in bearings may be divided for signature-analysis purposes into two general categories: (1) discrete defects, such as dented balls, scratched or brinelled races; and (2) distributed defects, such as out-of-roundness, race waviness, or unequal ball forces. Dynamic effects, such as retainer instability, appear as modifications of these basic signature phenomena. The third, and most important, bearing problem - lubricant failure - also manifests itself in modifications of the basic bearing signature, but the nature of lubricant failure does not lend itself to analytical treatment. Past experimental results, however, have indicated the feasibility of detecting lubricant failure through signature indications.

As stated earlier, the Acoustic Signature Analysis method is based on correlating the self-generated vibration signature of a bearing or bearings (suitably recorded, analyzed, and displayed) with the analytically predicted signatures of a normal unit, and of units containing various defects. The gross signature of a discrete-bearing defect is the impact repetition rate, which may be predicted from known relationships describing the relative motion of bearing parts. This simple model is not sufficient to explain the observed acoustic signatures, however. The manner in which even gross signature indications are transmitted from a bearing part to a transducer external to the device is highly dependent upon loading conditions and upon the nature of the intervening structure. In addition, there is considerable interaction between defects within a bearing; and most defects are always present to some degree, however slight. This complexity underscores the importance of a thorough understanding of the mechanisms of vibration generation and propagation.
The discrete-defect signatures previously discussed may be considered as special cases in the general bearing model that has been developed. This model predicts the dynamic deflections of the races which result from the action of a system of forces transmitted between inner and outer race by the rotating balls. In the model, these forces can be sinusoidally varied as a function of the rotational angle of any of the bearing elements. Once a solution for a simple sinusoidal variation is obtained, of course, any arbitrary dimensional variation with rotational angle can be synthesized as a Fourier series. It can be shown, for example, that a bearing with an out-of-round race will generate certain vibration frequencies that do not appear in the signature of a "normal" bearing. The presence of these frequency components in the measured signature of an electromechanical device (such as a gyro or reaction wheel) is therefore an indication that the component contains an out-of-round bearing. Similarly, characteristic signature indications are generated by other types of defects, such as brinelled races, scored balls, etc. Note, however, that the defect indication is not typically the simple presence of a particular frequency component or components in the signature. More generally, a defect is indicated by the amplitude, frequency variation, or harmonic content of a "family" of signature components.

The mathematical model also takes into account: (1) interactions between the signature components generated by multiple defects, and (2) the various modes of propagation of acoustic energy from bearing elements into the surrounding structure.

Because of the vast number of possible defect combinations, and because of additional complexities introduced by structural and instrumentation characteristics, the interpretation of an observed signature in terms of even geometric defects cannot be a simple matter of matching with a predicted model. Load variations, dynamic instabilities, and lubricant-degradation phenomena add further complications. The development of the Acoustic Signature Analysis process, therefore, has depended heavily on experience, and a continuing correlation of empirical data with the mechanisms of signature generation and propagation as revealed by the math modeling work. A set of guidelines that have been translated into usable test criteria have emerged, however, and have been successfully applied to screen gyro's for flight worthiness.

A Discussion of Some Specific Applications - Narrow-band Acoustic Signature Analysis has been applied successfully to small, high-speed gyro's, in two separate programs. In both cases the data were taken in the gyro vendor's plant and returned to GE for analysis. Each gyro was analyzed at the wheel level. Although several vendors are involved, all gyro wheels are mounted on R-2 size ABEC-7-9 angular contact ball bearings. In one study, involving 9 gyro's, the ASA performance definition was correlated with the results of an exhaustive tear-down analysis. Table 1 summarizes the results of the correlation. In general, 80% correlation was obtained. ASA was successful in identifying 100% of the good units. Note, in particular, that ASA shows good fidelity in identifying race and ball damage, both defect categories that can be environmental in origin and can be introduced by mishandling at any point up to launch.

A second study, involving 32 units, was not subject to such thorough tear-down. This study is significant in that the units were rated for flight-worthiness based upon defect severity distributions. These distributions were generated from ASA data for the following important defect categories: preload/wear, race
<table>
<thead>
<tr>
<th>GYRO</th>
<th>ESSENTIAL SA CONCLUSIONS</th>
<th>TEAR-DOWN RESULTS</th>
<th>CORRELATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OVERALL CONDITION - 4_T</td>
<td>CONFIRMED</td>
<td>YES</td>
</tr>
<tr>
<td></td>
<td>LOW RACE DAMAGE</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO SIGNIFICANT UBF</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO/POSSIBLE BALL DEFECT</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SOME OOR (M = 2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MODERATE IMBALANCE 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO SIG ORD/SEVERE ORD</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SIGNIFICANT UBF/WORST UBF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO BALL DEFECT</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SIG MISALIGN (OOR M = 1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SIGNIFICANT 3-LOBE OOR</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SIGNIFICANT IMBALANCE 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>OVERALL CONDITION - 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SEVERE BALL SLIP (HIGH β)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>WORST RACE DAMAGE</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SIGNIFICANT UBF</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HIGH PRELOAD</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SOME OOR (M = 1, 3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>OVERALL CONDITION - 3_T</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LOW RACE DAMAGE</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HIGH PRELOAD</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO OOR</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NORMAL UBF</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- E - Essential
- F - Further
- G - General
- H - Highest
- T - Teardown

**Correlation:***
- YES
- NO
- NO/YES
Fig. 2  OVERALL FLIGHT WORTHINESS RANKINGS
damage: ball damage; unequal ball forces; imbalance; contact angle. A given distribution consists of the sum of defect severity indices calculated from the ratios between relative levels of groups of peaks for a given signature component. More than one severity index is calculated for each defect category. For example, race damage can give rise to several different spectral anomalies. An index is computed for each. The defect severity distribution is the average of these indices. The individual distributions are then combined to obtain the flight worthiness distribution shown in Figure 2. Note how the distribution is skewed toward the better units. Present success could be based upon this distribution - future success in long mission could require the judicious selection of the 90th percentile units and the continuous monitoring of environmentally-induced defects right up to the pad.

Research and development in ASA is in progress in two major areas: real-time analysis of transients, and ASA of bearings as components.

Real-time analysis, using a spectrum analyzer, has been applied to the acoustic analysis of the effects of slewing on a large control moment gyro. This approach has been promising, with preliminary data indicating that the spin axis is cocking or that the bearings are being forced out-of-round by the dynamic loads. An important conclusion from this work is, that while real-time broad-band analysis is an extremely useful tool for the analysis of transients, narrow-band analysis with careful mathematical modeling of steady-state spectra is required for proper interpretation of the transient spectra.

Component-level tests have been carried out on R4 bearings from two different vendors, built for two completely different applications. The bearings were dead-weight thrust loaded in an "ideal" installation. The acoustic spectra were, in general, very uniform with remarkable similarity. Differences were revealed only by subtle indications not evident in the general appearance of the frequency-amplitude plots. This was surprising in view of the high variability in condition of bearings installed in such diverse devices as gyros, momentum wheels, tape recorders and horizon scanners. Two conclusions are possible: mathematical modeling and narrow-band ASA are essential to the acoustic screening of precision bearings as components and installation and handling appear to be responsible for a great deal of bearing degradation.

DISCUSSION - The General Radio frequency spectrum analyzer was reported to be used. The mathematical model used for calculating a reference signature provides relative amplitude versus frequency spectrum for each defect category. Miller questioned whether any useful information (regarding mechanical condition) had been found in very high frequency ranges such as those representing ball resonance. Although Snediker reported no practical interest in that range, it was noted from the audience that Boeing is getting useful information in the megahertz range. The very high frequency signals attenuate rapidly, so that it is difficult to transmit them out of a mechanism through an oil film. Schlereth suggested that this fact might be used as a simple check on the effectiveness of lubrication; if the very high frequency signals from internal elements were transmitted out, it would suggest rupture of the oil film. Schlereth also reported having listened to gear tooth vibration in the 100 kilocycle range. M.T.I. is looking for an air path to transmit such signals, perhaps via a
transmitter moving with the gear teeth. To Glassman, Snediker recommended sealing shipboard mechanisms which suffered bearing damage at the hands of the maintenance people. To Stern's question of the change in signature between a class 5 and class 7 bearing, the author indicated that he had never looked at the acoustic signature of a ball bearing worse than class 7.

11A. The meeting recessed for the day at 5:30 p.m. It reconvened at 9 a.m. on April 27 for the fourth technical session with Dr. F.F. Ling, Director, Institute for Wear Control Research, Rensselaer Polytechnic Institute as Chairman.


Foreign Object Damage (FOD) in jet engines is a major flight safety and maintenance problem to the military. Few objects which damage the engines are identified, but typical damage is caused by runway surface debris or by objects left or failed within the air inlets. The inspection and checkout of compressor rotor blades on an engine installed in the aircraft is generally a difficult and time-consuming problem at best. Normally, FOD is not found until it severely affects engine performance in flight. Hence, there is a need to detect FOD before its results cause a major engine failure, especially in flight or on the flight line, without the need for disassembly. The objective of the activity described was to determine the feasibility of doing this.

Since most of the blade damage appears on the leading edge, this FOD could be detected by noting leading-edge defects. Damage near the root of the blade frequently results in crack development and ultimate failure. A precursor of this failure can be detected by noting abnormal twisting or bending of the blade. Another similar type of blade failure is frequently initiated by localized areas of corrosion. These can cause crack development in highly stressed portions of the blade and can also be detected in advance of failure by noting abnormal blade bending, especially under full aerodynamic loading.

The aforementioned approaches were developed as a part of a broadly-based feasibility program. The ideas and services of a wide number of engineers and scientists with various backgrounds and training were drawn upon early in the program. The program was initiated with an examination of over forty possible physical effects or phenomena. Then seven techniques were selected for analysis, as given in Table 1. The more promising techniques were then experimentally evaluated on a simple simulated compressor section which resembled a table-top fan. After these initial laboratory breadboard tests, only two techniques - the millimeter-wave interferometer and eddy-current detector - appeared worthwhile for additional consideration as leading-edge-defect detectors.

These two techniques were then evaluated on a laboratory-mounted J-47 compressor section. Another technique was developed during tests on the compressor section. It was discovered that the blades were magnetic and that if any one of these blades were struck by an object to cause a defect, it would be permanently demagnetized.
### Table 1
**Techniques Investigated in Depth**

<table>
<thead>
<tr>
<th>Selection</th>
<th>System</th>
<th>Type of Defect Detected</th>
<th>Current Analytical or Experimental Results</th>
<th>Future</th>
<th>Field Usage</th>
<th>Recommendation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millimeter-Wave</td>
<td>Interferometer</td>
<td>Leading edge defects on 1st and 2nd stages. Defects on airfoil contour area of 1st stage.</td>
<td>Detected 0.03&quot; radius defects</td>
<td>Higher frequency system should resolve 0.005&quot; leading edge defects. Also larger defects on airfoil contour area of 1st stage and edge defects on 2nd stage.</td>
<td>Small probe inserted into cowling for flight-line checkout.</td>
<td>Suitable for flight-line tests after development of higher frequency system.</td>
</tr>
<tr>
<td>Electrometer</td>
<td></td>
<td>Leading edge defects, 1st stage</td>
<td>Insufficient resolution</td>
<td>-</td>
<td>-</td>
<td>Drop</td>
</tr>
<tr>
<td>Eddy-current Techniques</td>
<td></td>
<td>Loading edge defects, 1st stage</td>
<td>Subject to normal axial position variation of blades</td>
<td>-</td>
<td>-</td>
<td>Drop</td>
</tr>
<tr>
<td>Magnetic Field</td>
<td>Techniques</td>
<td>Blade or leading edge defects, 1st stage</td>
<td>Subject to normal axial position, and variation of blade. Less sensitive than eddy-current techniques.</td>
<td>-</td>
<td>-</td>
<td>Drop</td>
</tr>
<tr>
<td>Optical Technique</td>
<td></td>
<td>Loading edge or airfoil contour area defects</td>
<td>Subject to field usage problems, such as false alarms due to oil spots.</td>
<td>-</td>
<td>-</td>
<td>Drop</td>
</tr>
<tr>
<td>Eddy-Current Blade</td>
<td>Tip Parameter Monitor</td>
<td>Detects a hit blade on any row by noting disappearance of remnant magnetization.</td>
<td>Detected blade which was hit to cause a 0.015&quot; radius defect.</td>
<td>Ready to be extended to feasibility broad-board.</td>
<td>Small unit mounted in shroud above stages for all engines employing magnetic compressor blades.</td>
<td>Consider for in-flight monitoring, especially during takeoff or near bird flyways. Can use for flight-line tests as well.</td>
</tr>
<tr>
<td>Remnant Magnetic Field</td>
<td></td>
<td>Detects significant hits or crack development by noting blade twist or bending.</td>
<td>Detected blades which were twisted or bent by a hit capable of causing a 0.05&quot; radius defect.</td>
<td>Ready to be extended to feasibility broad-board.</td>
<td>Small unit mounted in shroud above row of blades to be monitored.</td>
<td>Consider for in-flight monitoring to grow about 1 hour warming of excessive crack development. Can use on flight-line as well.</td>
</tr>
</tbody>
</table>
DUAL ANTENNA INTERFEROMETER TEST SETUP

Figure 1

Reproduced from best available copy.
Figure 3

RELATIVE HOLE SPACING AND CLEARANCE HOLE REQUIREMENTS FOR BLADE TIP DETECTOR
An analysis of the specified tolerances, relative to blade positioning and rework, indicated that the smallest variations occurred at the blade tips. Tests and analyses also demonstrated that significant damage or crack development resulted in one or more of the tip parameters exceeding the specified tolerance limits by a large value. By suitable tip-parameter sensor design, important evidence of FOD or crack development can be monitored. To demonstrate this, an eddy-current sensor was placed in a small hole in the shroud above the row of rotor blades to be monitored. This sensor system was designed to detect overall twisting or bending at the blade tip. While subjected to a number of qualifications, breadboard tests on the J-47 compressor indicated that damage was easily detectable.

The program demonstrated the potential of three techniques to detect FOD, as summarized in Table 1, and no major problem areas of critical experiments were identified. Thus, all aspects appropriate to a feasibility investigation were found favorable for these three systems. Therefore, it was recommended that an exploratory model of a tip-parameter sensor be developed. Further development of the millimeter-wave interferometer system, as shown in Figure 1, was considered as a flight-line test technique to determine the extent of FOD by locating the position and size of the defect.

The exploratory model system, in Figure 2, has shown the capability for detecting tip curl, blade-tip twist, and blade-tip-to-blade-tip spacing which exceeds the normal engine tolerances of these quantities on the J-47 compressor at monitoring speeds and on the J-57 engine from idle to 90 percent power, with the detector configuration shown in Figure 3. While this type of FOD blade deformation is only a percentage of total FOD found on blades, it is believed that a strong correlation between this detectable damage and the total extent of FOD does exist. The extent that this is true for all engines, however, must be established before this system can serve as a reliable indicator of total compressor FOD. A survey of U.S. Air Force jet engines indicated the detectors can function in the J-57, J-75, TF-33, J-79, and J-85 engines, although structural analysis of the sensor modification requirements is necessary.

At this point in the development of an FOD detection system, an exploratory model in-flight and flight-line system has been demonstrated as capable of detecting the class of FOD resulting in distortion of the blade-tip geometry. Prior to any engineering applications to specific engines, the logical continuation of this effort would include a more comprehensive FOD analysis program.

The continued development of the FOD detector is important because the system offers a valuable tool in the determination of engine status. It is believed that the continued FOD development will provide an FOD diagnostic system to positively identify FOD difficulties which will, in turn, lead to considerable savings in both time and money at overhaul and maintenance facilities. Furthermore, the FOD detection instrument is believed to be a key element in the system for complete in-flight assessment of engine performance.

DISCUSSION - The capabilities and limitations of the prototype detector were brought out. Successful operation at full power has been obtained in the J-57. No effort has been made to detect blade resonance (when it occurs) or rotating compressor stall, but both should be possible. Sensor-to-tip separation is about 60 mils. Although test installations were made in the first few rows, service
installations would probably cover the last stage or two, where damage anywhere in the compressor should show up. Temperature capability was indicated to be that normally encountered in compressors. Gardner suggested basic similarities in the IITRI and Bendix programs; they are both based upon logic circuits to indicate when a flaw is detected, but are separately supported for differently-oriented users. Reason for rejection of the eddy current principle was its sensitivity to normal axial position variations of the rotor.


The failure by fracture of stressed metals in corrosive environments [Stress Corrosion Cracking (SCC)] is one of the major factors limiting the use of metals in a desired medium. SCC is a highly interdisciplinary phenomenon, involving a critical mix of metallurgical, mechanical, and chemical (electrochemical) factors in order to take place. The last factor, which includes environmental composition, effect of surface films, and electrochemical potential, determines the role that environment plays.

This talk focuses its attention on the role environment plays in determining the susceptibility of a stressed metal to cracking and therefore assumes that the mechanical and metallurgical conditions for cracking are met when the effects of environment are examined. It explores mechanisms which attempt to explain how an environment affects SCC in order to be able to predict susceptibility to failure in an environment where SCC behavior is unknown, assuming that the development of a useful mechanism guides one in producing diagnostic tools which allow one to assess the prognosis for failure.

Mechanisms - The mechanisms most frequently proposed for SCC are the following: 1) film rupture mechanism; 2) mechano-chemical mechanism; 3) stress-sorption mechanism; 4) brittle film mechanism; and 5) hydrogen embrittlement mechanism. This talk describes the role that environment plays in each of these mechanisms and discusses the major problems inherent in each of them.

Film Rupture Mechanism - This mechanism, suggested by Logan (1) and Champion (2), proposes that the protective film present on a metal surface (if it were not there the metal would fail by corrosion alone) is ruptured by continued plastic deformation at a crack tip where the exposed bare metal becomes an anode and metal dissolution takes place. The rest of the metal surface, especially the walls of the crack, acts as a cathode. Susceptibility depends on the rate at which the metal exposed by film rupture is repassivated vis a vis the rate of metal dissolution. Environment has an effect on the rate of repassivation because it affects the composition of the film formed and because it affects the electrochemical potential of formation. Environment also affects the mechanical properties of the film (its ability to fracture). A major problem with this mechanism is that cracking has been observed in systems where films are thought not to be present. Recent experiments (3) indicate that films can exist in systems where they would not be expected from a thermodynamic basis. Another problem is that cracks have been observed propagating from a surface which is dissolving at a high rate.
Mechano-chemical Dissolution Mechanism - This mechanism proposed by Hoar and Ullis (4) bears some similarities to the one just discussed in that the crack tip becomes an anode where dissolution takes place. But the difference in potential between the crack tip and the crack walls (cathode) is not due to the presence of a film. Instead, the crack tip is anodic because the deformed metal has a greater tendency to dissolve than the less deformed metal elsewhere.

The rate of dissolution is

\[ i_a = A n \exp \left( \frac{-\Delta G}{RT} \right) \exp \left( \frac{\alpha ZF\eta}{RT} \right) \]

where environment affects \( \Delta G \), the free energy of activation for dissolution and \( \eta \), the overpotential for dissolution. "A" is a constant; "n", the density of dissolving sites of the surface (affected by stress); \( \alpha \) is the fraction of \( \eta \) that assists the dissolving ions over the energy barrier; \( Z \) is the number of charges; and \( F \) is Faraday's constant. The main problems with this mechanism are that it is difficult to rule out the existence of films in most cases and the effect of environment on \( \Delta G \) and \( \eta \) is much less than the effect of strain on \( n \). Therefore, specificity of environment is more difficult to explain using this mechanism.

Stress-sorption Mechanism - This mechanism, most actively advocated by Uhlig (5), proposes that a specific species adsorbs and interacts with strained bonds at the crack tip causing a reduction in bond strength or, thermodynamically stated, a reduction in the surface energy, leading to a lowering in the stress required to produce brittle fracture. Uhlig has proposed that the effect of potential on SCC susceptibility arises because adsorption is potential dependent. Environment plays a role in this mechanism because of the specificity of adsorption of a given species on a given surface and because environment fixes the potential at a value where adsorption can or cannot take place. One problem with this model is that for most alloys their ductility is sufficient to produce extensive plastic deformation at a crack tip. The blunting that this produces eliminates the infinite sharpness required for this mechanism to work. Another problem is that the large amount of metal dissolution observed in many experiments makes this model seem unlikely - the metal dissolves out from under the adsorbed film.

Brittle Film Mechanism - This mechanism, first developed by Forty (6), suggests that SCC occurs because the environment produces an embrittled surface layer which undergoes brittle fracture when tensile stress is applied. The crack produced enters the ductile metal below this layer and a new film is formed on the bare metal so produced. The process continues by a repetition of the film fracture-reformation cycle. Environment affects this model via its influence on the film formation kinetics and its influence on the mechanical properties of the surface layer. For some systems the evidence speaks strongly for the model, e.g., the finding of striated fracture surfaces indicating a cyclic process. For other systems where the crack rate is low, where striations are not observed, and where extensive metal dissolution is known to occur during cracking, the model does not appear to be applicable.

Hydrogen Embrittlement Mechanism - This is considered by some to be a different phenomenon than SCC, but since cathodic reactions (which produce hydrogen under the proper conditions) are as much a part of corrosion as anodic ones (producing films and/or metal dissolution), it is difficult to exclude it in a general treatment of the role of environment on SCC. This mechanism operates by the production of a brittle region at the crack tip by means of the introduction of hydrogen into...
Fig. 1 TRIBO-ELLIPSOMETRIC APPARATUS. THE POLISHING WHEEL REMOVES EXISTING FILMS ON A METAL SURFACE AND THE RATE OF REPASSIVATION IS MEASURED BY HIGH SPEED ELLIPSOMETRIC TECHNIQUES. SIMULTANEOUSLY THE CURRENTS INVOLVED IN REPASSIVATION AND METAL DISSOLUTION ARE MEASURED USING THE COUNTER ELECTRODE, THE REFERENCE ELECTRODE AND A POTENTIOSTAT (FROM 11).

Fig. 2 COMPARISON OF THE CHARGE TO THICKNESS RATIO FOR REPASSIVATION OF MILD STEEL IN SODIUM NITRITE AND SODIUM NITRITE SOLUTIONS AS PLOTTED AGAINST TIME AT 85°C. THE STEEL IS SUSCEPTIBLE IN THE NITRITE AND NOT SUSCEPTIBLE IN NITRITE. (FROM 11).
the metal via cathodic reactions or by other ways. The environment can affect
the process by influencing the rate of proton production and by enhancing or
inhibiting the entry of \( H_2 \) into the metal through the interposition of adsorbed
layers or reaction layer films. The main problem preventing this mechanism from
being a universal one for SCC is that a number of experiments have shown that,
under conditions where hydrogen has been known to enter the metal, no SCC occurs,
while under other conditions for the same system where \( H_2 \) does not enter, SCC
occurs readily.

**Experimental Approaches to Predictability** - In order to determine which mechanism
is operative for a given SCC system and predict susceptibility for a given
system, a number of new experimental approaches have been or are being developed.
These include occluded cell chemistry (7), electro-chemistry of straining elec-
trodes (8,9), and scraped electrodes (10) and tribo-ellipsometry (11). These
experimental tools designed using the above mechanisms as a guide promise to
throw light on the phenomenon of SCC and to provide tools for predicting the
probability of failure in a given environment. Tribo-ellipsometry apparatus
and the sort of results it produces are shown in Figs. 1 and 2.

**REFERENCES**

When some metals are subjected to tensile stresses in certain chemical solutions of the proper concentrations, cracking can occur with no visible plastic strain at a fraction of the normal tensile strength. The tensile stresses may be imposed by external loads or by internal residual stresses created by heat treatment, welding or cold work. The cracking may be intergranular or transgranular, depending on the material and the temperature, the stress level, and the medium involved.

As a result of sporadic instances of stress corrosion cracking in a number of large steam turbines during the past decade, the author's company initiated a program several years ago to determine the relative susceptibilities to these phenomena of a number of metallic materials in common use in turbine construction. The program was also directed toward determining the order of magnitude of the stress levels that must not be exceeded to avoid cracking in the corrosive media that have been encountered in some steam turbines.

Service Experience - The general design features, materials and steam conditions in the turbines which suffered stress corrosion cracking are tabulated in Table I. There have been additional cases of stress corrosion cracking in expansion bellows made of austenitic stainless steel, in low-alloy bolts, and in martensitic stainless steel bucket covers and tie wires. Although these instances have been rare - and apparently associated with unusual combinations of feedwater treatments, carry-over problems, material conditions, and design - they indicated a need for more quantitative information concerning the behavior of turbine materials in corrosive environments to provide turbine designs as resistant as possible to stress corrosion cracking, and also to provide turbine owners with better evidence of the need for avoiding the introduction of harmful contaminants. We believe that the service experience with the sodium sulfite feedwater treatment and the cracking which had been demonstrated in samples subjected to sulfite-treated steam at only moderately high stress levels amply demonstrated that this practice should be avoided in boilers operating over 900 psi. Apparently, hydrazine has been demonstrated to be as satisfactory an oxygen scavenger as sodium sulfite, with no deleterious effects. The case for caustic is not as clear-cut because many turbines have operated satisfactorily in spite of caustic deposits. There apparently is not a suitable feedwater treatment available which will give positive assurance against the introduction of caustic, especially when there are condenser leaks introducing large quantities of contaminants that cannot be handled satisfactorily with the zero solids treatment.

Accordingly, an extensive laboratory program was initiated to study the behavior of a wide range of turbine materials in caustic. It was decided to conduct the tests at the temperature and caustic concentration representative of that occurring near the dew point in a modern reheat turbine. The condition frequently occurs at the next-to-last stage in the low-pressure section at about 150°F and
### TABLE I

**GENERAL DESIGN FEATURES, MATERIALS AND STEAM CONDITIONS IN TURBINES WITH STRESS CORROSION CRACKING**

<table>
<thead>
<tr>
<th>Source of Corroding Medium</th>
<th>Turbine Type</th>
<th>Location of Cracks</th>
<th>Material</th>
<th>Steam Conditions at Crack Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Dilute&quot; caustic wash</td>
<td>1800-rpm, single-shaft, condensing</td>
<td>Shrink on wheels</td>
<td>1Cr-1/2Mo steel</td>
<td>752F/440F, 185/28.7 psia</td>
</tr>
<tr>
<td>Caustic steam treatment</td>
<td>3600-rpm, 3-shaft, triple-exhaust, single-reheat</td>
<td>L-1 wheel fillet</td>
<td>1Cr-1Mo-1/4V solid rotor</td>
<td>140F, 2 psia</td>
</tr>
<tr>
<td></td>
<td>3600-rpm, single-shaft condensing boiler feedpump</td>
<td>Dovetail hooks</td>
<td>2-1/2Ni-1Cr-1/2Mo-1/10V</td>
<td>300F/220F, 150/14 psia</td>
</tr>
<tr>
<td>Hydrogen sulfide from sodium sulfite feedwater treatment</td>
<td>3600-rpm, 2-shaft, double-exhaust, single-reheat</td>
<td>Rubbed area between L and L-1 wheels</td>
<td>2-1/2Ni-1/10V solid low-pressure rotor</td>
<td>148F, 2.2 psia</td>
</tr>
<tr>
<td></td>
<td>3600-rpm, 2-shaft, double-exhaust, condensing</td>
<td>Dovetail hooks L and L-1 wheels on HP turbine rotor</td>
<td>1Cr-1Mo-1/4V solid HP rotor</td>
<td>243F/227F, 2.3/18 psia</td>
</tr>
</tbody>
</table>

### TABLE II

**MATERIAL CHEMICAL COMPOSITION**

<table>
<thead>
<tr>
<th>Alloy Identification</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Other</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.23</td>
<td>0.29</td>
<td>0.010</td>
<td>0.013</td>
<td>0.03</td>
<td>3.48</td>
<td>1.75</td>
<td>0.39</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.24</td>
<td>0.38</td>
<td>0.010</td>
<td>0.011</td>
<td>0.24</td>
<td>3.15</td>
<td>0.14</td>
<td>0.34</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.31</td>
<td>0.71</td>
<td>0.007</td>
<td>0.007</td>
<td>0.27</td>
<td>0.23</td>
<td>1.24</td>
<td>1.20</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.28</td>
<td>0.67</td>
<td>0.010</td>
<td>0.013</td>
<td>0.18</td>
<td>1.85</td>
<td>1.27</td>
<td>0.54</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.28</td>
<td>0.34</td>
<td>0.011</td>
<td>0.010</td>
<td>0.22</td>
<td>3.38</td>
<td>1.67</td>
<td>0.57</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.44</td>
<td>0.57</td>
<td>0.014</td>
<td>0.011</td>
<td>0.29</td>
<td>-</td>
<td>0.95</td>
<td>0.52</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.13</td>
<td>0.40</td>
<td>0.017</td>
<td>0.028</td>
<td>0.21</td>
<td>0.35</td>
<td>11.86</td>
<td>0.18</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.24</td>
<td>0.65</td>
<td>0.009</td>
<td>0.003</td>
<td>0.08</td>
<td>0.91</td>
<td>10.73</td>
<td>0.63</td>
<td>0.15</td>
<td>0.85W</td>
</tr>
<tr>
<td>9</td>
<td>0.038</td>
<td>0.47</td>
<td>0.012</td>
<td>0.011</td>
<td>0.49</td>
<td>0.30</td>
<td>13.98</td>
<td>-</td>
<td>-</td>
<td>0.15Al</td>
</tr>
</tbody>
</table>
2.0 psi. Since the equilibrium concentration of caustic under these steam conditions is 28 percent, the tests were conducted with this concentration at 150°F. The pressure was atmospheric, but this higher pressure is not believed to have significantly affected the corrosion results.

Test Procedure - Although it is common to use bend type tests in stress corrosion cracking investigations, the determination of the stress distribution in such samples is not precise. Since one of the major purposes of this study was to determine the relationship between time-to-cracking and stress level, the bolt type test specimen shown in Figures 1 and 2 was developed. A calibration of elongation versus stress was obtained for each material, using strain gauges attached to the specimens. The test stress applied to each specimen was determined by tightening the nuts and measuring the over-all bolt length. The specimen length was again measured after test to ensure that the bolts had not relaxed. It is estimated that the stresses imposed in this manner were within ±5 percent of the calculated value.

The specimen and the fixture were of similar material to avoid thermal expansion stress and galvanic effects. Before assembly the test specimens were washed with acetone and deionized water. The carbon steel vessels in which the tests were conducted were also washed by deionized water flowing at a low rate for 24 hours before the test. The caustic solutions were prepared from reagent grades of sodium hydroxide and demineralized water (resistivity 10 megohm-cm or higher at room temperature). The chloride content of the test solutions after test was always less than 3 ppm. The specimens were examined metallographically for cracks in the as-polished and etched conditions.

Fig.1 SKETCH SHOWING DIMENSIONS OF THE SMOOTH-BAR AND NOTCHED-BAR STRESS CORROSION SPECIMENS.
Table II lists the chemistries of the materials tested and Table III lists the mechanical properties. Alloys 1, 2, 4 and 5 have been commonly used for low-pressure rotor and buck-wheel; alloy 3 is representative of the currently used high-pressure, high-temperature rotor material which in older designs carried some stages operating in the wet regions of the turbine. Alloy 6 is similar to ASTM A193 Grade B16 used in bolting applications. Alloy 7 is Type 403 turbine quality 12 percent Cr steel used for turbine buckets and bucket covers. Alloy 8 is similar to ASTM A437 Grade B4B used for high-temperature turbine bolting and alloy 9 is essentially AISI Type 405 used in some instances for diaphragm partitions. The test results are presented in Table IV.

Discussion of Laboratory Tests - A comparison of Tables III and IV shows that all of the materials tested cracked in the 28 percent caustic solution within.
24,000 hours at stresses a fraction of their 0.02 percent yield strength. Although no "threshold" stress below which cracking will occur has been established by these tests, even the most optimistic extrapolation would indicate that the "safe" level of stress in these materials in caustic solutions is extremely low - certainly below the values necessary for the reasonable design of modern large steam turbines. Additional tests are necessary to provide a determination of the threshold stress levels of the various materials and to explore the effects of temperature and concentration on time-to-crack.

It may be argued that the results of the laboratory tests are not consistent with general service experience, since many units observed to have caustic deposits have not experienced cracking. Possibly the actual concentration of caustic in the early moisture region is somewhat less than the 28 percent solution used in these tests, or it may be that other contaminants in the steam tend to inhibit the corrosion compared to the pure chemicals used in these experiments. It may also be the case that in the units having caustic deposits that have not cracked, the service times have not been sufficiently long for cracking to occur in the particular materials and at the stress levels imposed.

**TABLE III**

**MATERIAL PHYSICAL PROPERTIES - ROOM TEMPERATURE (0.505 DIAMETER TEST SPECIMENS)**

<table>
<thead>
<tr>
<th>Alloy Identification</th>
<th>Tensile Str.-KPSI</th>
<th>0.02% YIELD Str.-KPSI</th>
<th>Percent Elongation</th>
<th>%Red. Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>116</td>
<td>94.5</td>
<td>22</td>
<td>69</td>
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<tr>
<td>2</td>
<td>101</td>
<td>79</td>
<td>21.5</td>
<td>56.2</td>
</tr>
<tr>
<td>3</td>
<td>108.5</td>
<td>87.3</td>
<td>20.5</td>
<td>57.1</td>
</tr>
<tr>
<td>4</td>
<td>116</td>
<td>97</td>
<td>24</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>147</td>
<td>120</td>
<td>19</td>
<td>59</td>
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<tr>
<td>6</td>
<td>127</td>
<td>123</td>
<td>23</td>
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<tr>
<td>7</td>
<td>108</td>
<td>78</td>
<td>22</td>
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</tr>
<tr>
<td>8</td>
<td>147</td>
<td>115</td>
<td>16</td>
<td>44</td>
</tr>
<tr>
<td>9</td>
<td>81.8</td>
<td>31.2</td>
<td>32</td>
<td>66.2</td>
</tr>
<tr>
<td>Alloy Identification</td>
<td>Stress PSI</td>
<td>Time Hours</td>
<td>Cracks Detected</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>------------</td>
<td>------------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
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<tr>
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<td>10,000</td>
<td>1,500</td>
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<td></td>
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<tr>
<td>1</td>
<td>3,600</td>
<td>24,000</td>
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<tr>
<td>2</td>
<td>79,000</td>
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<tr>
<td>3</td>
<td>87,000</td>
<td>1,400</td>
<td>No</td>
<td></td>
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<tr>
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<td>97,000</td>
<td>1,400</td>
<td>No</td>
<td></td>
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<tr>
<td>5</td>
<td>120,000</td>
<td>1,400</td>
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<td></td>
</tr>
<tr>
<td>5</td>
<td>78,000</td>
<td>2,600</td>
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<td>52,000</td>
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<td>6</td>
<td>123,000</td>
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<td>6</td>
<td>67,500</td>
<td>4,000</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>85,000</td>
<td>2,100</td>
<td>Yes</td>
<td></td>
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<tr>
<td>7</td>
<td>76,500</td>
<td>4,000</td>
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<tr>
<td>9</td>
<td>40,000</td>
<td>1,500</td>
<td>Yes</td>
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<tr>
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<td></td>
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<tr>
<td>9</td>
<td>30,000</td>
<td>4,000</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>20,000</td>
<td>24,000</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

Therefore, in spite of the successful operation of some units with caustic, it would seem prudent to make every effort to keep caustic out of turbines and to frequently inspect those units where caustic carry-over has been shown to be a problem.

**Conclusions** - The results of service experiences and laboratory tests reported herein indicate that:

1. Caustic washing of turbines even with dilute solutions should be avoided because, when evaporation occurs as the turbine heats up, the caustic solutions produced can be sufficiently concentrated to cause stress corrosion cracking.
2. The use of sodium sulfite as an oxygen scavenger should be avoided because it can produce hydrogen sulfide in the steam which can cause stress corrosion cracking.

3. Care should be taken to avoid caustic contamination of the turbine because the materials whose characteristics are suitable for turbine construction are subject to stress corrosion cracking at moderate stress levels.

4. Those units which are known to have a caustic carry-over problem should be subjected to frequent inspection, particularly in the vicinity of the early-moisture region of the turbine.

DISCUSSION - Yukawa reported that attempts had been made to identify contaminants on the intergranular fracture surfaces by direct microscopic analysis. Difficulty arises in the caustic may turn to sodium carbonate when it is exposed to air, with its CO\textsubscript{2} content. The cracks which occurred where packing rings contacted the rotor were reported to have originated in the heat-affected zone but spread through the virgin rotor material. The seal material itself was non-ferrous. Hamberg questioned whether the laboratory test findings had led to a change in turbine materials; Yukawa replied that few significant changes had been made since there were strong constraints at work. For example, the high pressure rotors are of chrome-moly-vanadium steel, formulated for essential high temperature creep strength; the very large forgings used dictate low-alloy steels.

15. "ENVIRONMENTAL EFFECTS ON MECHANICAL FAILURE INVOLVING PARTICULARLY MULTIPHASE FLOWS," by F.G. Hammitt, Professor of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan 48104.

Introduction - The subject of this presentation concerns mechanical failure involving particularly multiphase flows. This concerns in most general terms two major types of phenomena, i.e., those involving: a) primarily liquid flows; and b) primarily gaseous or vaporous flows. In each such category there are several technologically important damaging situations which are listed below.

1. Liquid Flows
   a) Liquid flow with entrained vapor bubbles (usually also with some gas content), i.e., cavitation.
   b) Liquid flow with entrained solid particles leading to ordinary erosion.
   c) Liquid material combinations where chemical reactions contribute substantially to material damage.

2. Gaseous and/or Vaporous Flows
   a) Primarily gaseous or vaporous high-velocity flows with entrained liquid droplets.
   b) Primarily gaseous or vaporous high-velocity flows with entrained solid particles.
   c) Gaseous or vaporous flows where chemical reactions with adjacent material surfaces are substantial.
Environmental Effects - Environmental effects upon material damage and failure are important in various ways in the situations outlined in the preceding paragraph. In more general terms these may be characterized as below, hopefully in probable order of importance:

1. Increased temperature of fluid and/or structure.
   a) Fluid-dynamic effects, particularly in the case of cavitation. The sensitivity of cavitation damage to temperature is primarily the result of rapidly increasing vapor pressure and density which lead to increased heat transfer restraints on bubble collapse (called "thermodynamic effects" in cavitation literature), as well as reduced collapsing pressure differential if system pressure is considered fixed.
   b) Reduced mechanical properties of materials at increased temperature.
   c) Increased chemical reaction rates leading to corrosive effects.
   d) Changes in other fluid properties with temperature such as primarily viscosity and surface tension.

2. Increased fluid velocity.
   a) Increased energy intensities, particularly in impact phenomena and cavitation.

3. Increased fluid pressure.
   a) The effect of increased fluid pressure is particularly important in cavitating liquid flows, where it is really a question of the difference between liquid pressure and vapor pressure, i.e., the suppression pressure. An increase in suppression pressure results in two conflicting trends, i.e., a diminution in number of cavitation bubbles, but an increase in violence of collapse. Figure 1 shows the effect for cavitation damage for a vibratory damage test facility where the second effect strongly outweighs the first, so that there is a strong increase in damage with suppression pressure in this particular case.

4. Scale Effects.
   a) Scale effects such as droplet size in aircraft rain erosion or cavitation bubble or "cavity" size. Some cavitating flows in fact involve macro-instabilities capable of creating gross structural damage to components such as propeller blades, hydraulic turbine blades, etc. (1).

Specific Examples of Environmental Effects - More specific examples of environmental effects upon material damage in multiphase flows were discussed. They are briefly summarized as follows:

1. Temperature and Pressure Effects - These are considered together because in those cases involving liquids they are essentially inseparable because of the importance of vapor pressure in the cavitation process and its direct dependence upon liquid temperature. Since the effects upon the fluid-dynamics of bubble collapse are probably of greatest importance they will be considered first. The experimental data (2,3,4) for a variety of fluids including high-temperature liquid metals from tests in vibratory damage facilities (the only systematic data presently available) were discussed, and application to flowing systems considered. Figures 1 and 2 summarize this data to some extent.
Fig. 1 MAX MDPR vs TEMPERATURE AND VAPOR PRESSURE FOR BEARING BRASS (SAE - 660)
FIG. 2. EFFECT OF THERMODYNAMIC PARAMETER ON CAVITATION DAMAGE - LIQUID METALS

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The relative importance of chemical and mechanical effects in many applications (such as high-speed surface ships operating in sea water) as they depend on environmental factors was discussed.

2. Velocity Effects - The effects of velocity include the increased energy intensities in impact due to higher velocities, and also the rather special effects in cavitation, where the effect of flow velocity depends essentially upon its effect upon pressure. Figure 3 summarizes velocity effects in a "rotating disc" cavitation damage test device (5). Increased velocity of course affects chemical corrosion rates which may be of particular importance where strong corrosive effects are present as in applications with sea water.

3. Size Scale Effects - The effects of size are important both in regard to impact phenomena where damage rates are extremely sensitive to the size of droplet or solid particle, and also in regard to cavity (or bubble) size in cavitating flows. These aspects were discussed in some detail.

4. Similarities Between Basic Phenomena Involved - Some mention was made of the basic similarities between impact damage and cavitation damage, and some relevant slides from the work of our own laboratory in this regard were shown.

![Fig. 3 CAVITATION DAMAGE VELOCITY EXPONENT](image)
REFERENCES


DISCUSSION - Sytko asked whether work had been done on the effect of gases dissolved in the liquids upon cavitation. Hammitt indicated that precautions were taken to limit the amount of dissolved gas, although there must always be some, and the content was measured. In general, presence of a lot of gas accentuates cavitation damage; a very small quantity retards cavitation through lack of nuclei; while in the intermediate range, effects are not significant. It was noted that no thorough study of the problem had been made.

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16. CLOSURE - Mr. Doroff expressed the thanks of all conference attendees to the NBS Boulder Laboratories for its fine hospitality and to the NBS Washington staff for its efforts with arrangements. On behalf of the Office of Naval Research, he thanked all participants for their interest and contributions from the floor; and the authors and session chairmen for their respective contributions. He announced that the next meeting, to be announced by NBS, would probably be held in Washington in about six months and would feature a technical program arranged by the DDP Committee. A major meeting about a year from now would attempt a broad overview of the entire mechanical failure problem area, leading perhaps to a "white paper" on the subject. With these announcements, he adjourned the formal meeting at 12:35 p.m., with a tour of laboratory facilities to follow at 1:30 p.m.
APPENDIX I

LIST OF ATTENDEES BEING COMPILED.