Effect of Organic Corrosion Inhibitors on Corrosion Fatigue

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INTRODUCTION

Organic corrosion inhibitors are commonly used by the oil industry to combat corrosion in various operations. In the primary production of oil, these chemicals are employed to protect the subsurface equipment against corrosive production fluids. Subsurface equipment such as sucker rods and pump parts are subjected to the combined action of cyclic service loads and corrosive fluids simultaneously. Such loading often causes failure due to corrosion fatigue. Organic inhibitors are widely used to prevent failure resulting from corrosion fatigue. There is, however, little or no data to show the nature and the extent of the effects they produce on the course of corrosion fatigue per se.

This investigation deals with some of the variables that affect the corrosion fatigue performance of carbon steels in the presence of organic inhibitors.

MATERIALS AND APPARATUS

Table 1 shows the chemical composition of the plain carbon steels used in these investigations. Table 2 shows the physical properties of the subject steels obtained by various heat treatments.

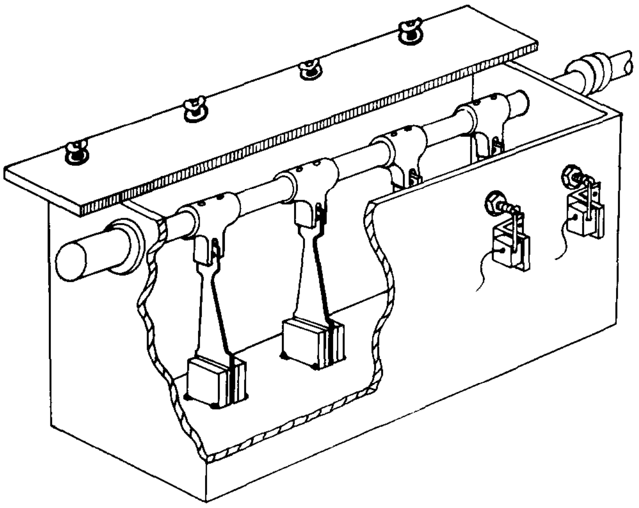


Figure 2 - Schematic Of The Corrosion Fatigue Apparatus

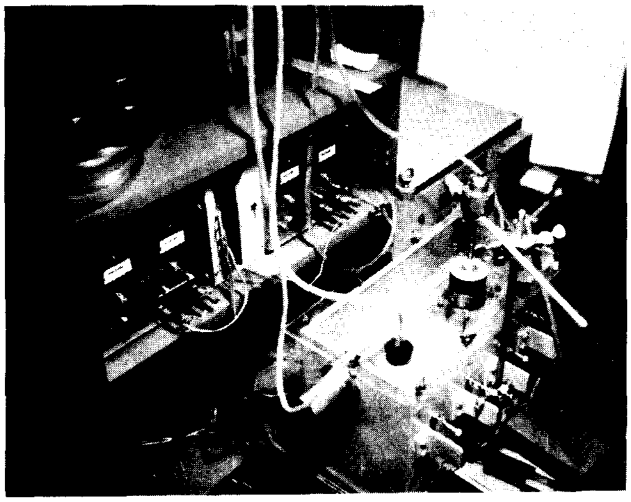


FIGURE 1

Figures 1 and 2 show the apparatus used for these tests. Details of the apparatus and testing procedures were discussed elsewhere.[3] It consists of a Monel tank in which four plate specimens are subjected to reverse bending in the environment of interest.

SALT WATER TESTS

It is necessary to briefly discuss the corrosion fatigue behavior of the subject steels in the environment of interest in order to provide sufficient background for the effects of the organic inhibitors. A more detailed discussion of the environmental effects is given elsewhere.[3] Two types of corrosive environments were selected

Table 1

Chemical Composition of the Steels

	C	Mn	Si	S	P
Sample (A)	0.34	0.55	0.06 (max)	0.04	0.03 (max)
Sample (b)	0.27	0.75	-	0.03	0.03 (max)

Table 2

Mechanical Properties and Heat Treatments

Steel Sample	Heat Treatment	Y.S.(psi)	U.T.S.(psi)	Hardness(Rc)
A_1	1600°F normalized	55,000	86,700	12-15
A_2	Oil quenched and tempered 1000°F	80,000	96,000	12-14
B_1	Oil quenched	73,000	95,000	12-15
B_2	Water quenched tempered 1000°F	104,000	112,000	22-26
B_3	Water quenched tempered 1050°F	90,000	101,000	20-24
B_4	Water quenched tempered 1200°F	75,000	88,000	14-16

for studying the effects of organic corrosion inhibitors:

(1) A 5 per cent sodium chloride solution saturated with CO_2. The solution contained about 2000 ppm CO_2 at a pH of 5.5-5.6. Figure 3 shows the corrosion fatigue performance of steel (steels A1 and A2) in this environment. These steels had air endurance limits of approximately 30,000 psi. In this environment the endurance limit was reduced by 41 per cent to a value of 17,000 psi.

(2) A 5 per cent sodium chloride solution saturated with a mixture of CO_2 and H_2S. Nitrogen was used as the diluting media to achieve a gas content of 60-70 ppm H_2S and 250-300 ppm CO_2 in the salt solution. The pH was 5.8. Figure 4 shows the corrosion fatigue curve of these steels (A1 and A2) in this environment. The endurance limit was lowered 62 per cent from that in air to a value of 11,600 psi.

It was believed that these two environments were representative of many of the severe corrosion fatigue problems encountered in production service.

EFFECT OF HYDROCARBON PHASE

In producing oil wells, metals are subjected to a mixture of hydrocarbons and salt water There is ample evidence that inhibitors perform differently with a hydrocarbon phase present. It was deemed desirable to determine the effects of a hydrocarbon phase on the corrosion fatigue properties of the steel specimens so that inhibitor evaluations could be made with this phase present. The hydrocarbon used in this study was Diesel fuel. The Diesel fuel and brine were mixed in a 50-50 ratio. A mixer (Fig. 2) and the movement of specimens provided enough mixing action so that the salt solution and diesel fuel were

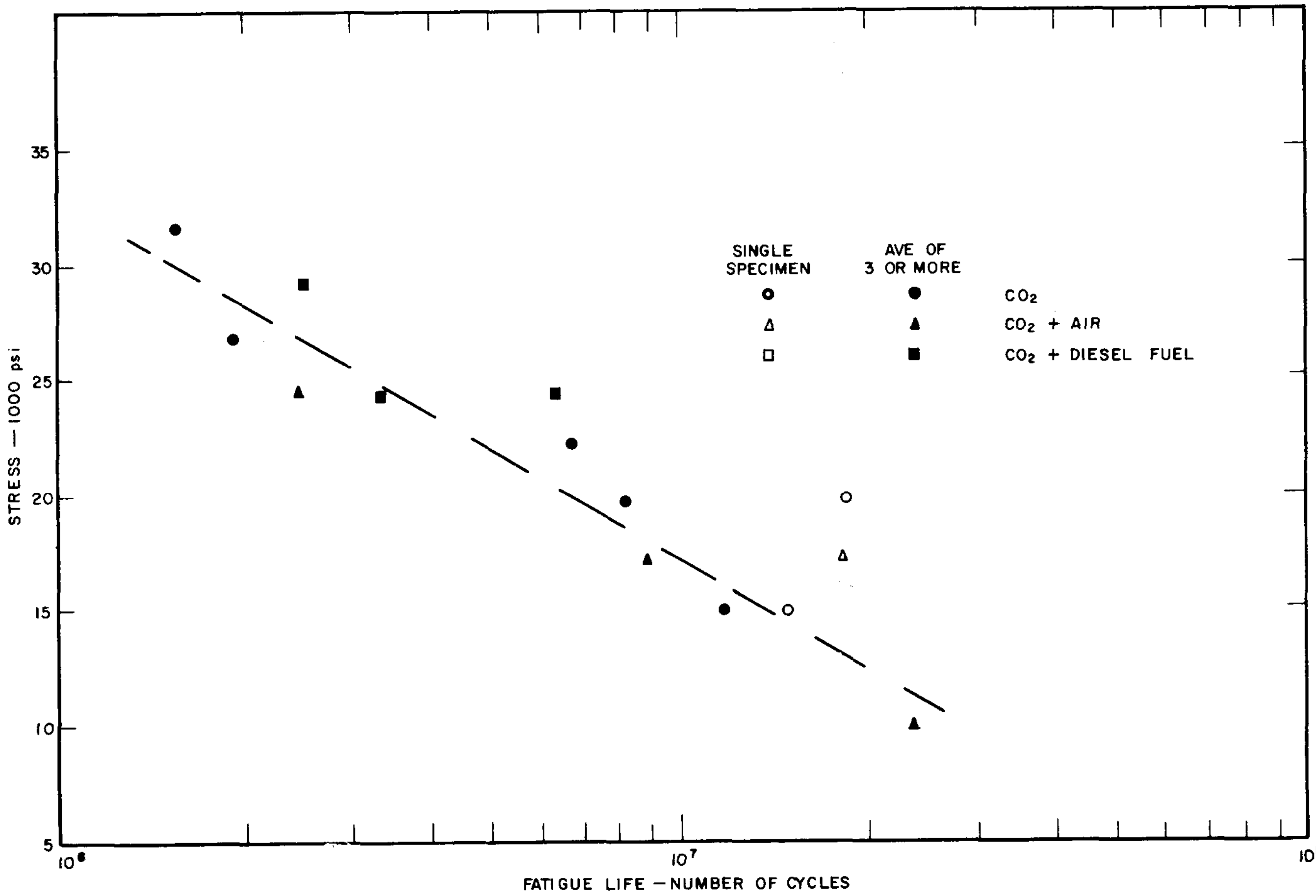


FIG. 3 CORROSION FATIGUE DATA
SALT WATER AND CO2

fairly well emulsified.

Figure 4 shows the effect of the Diesel fuel mixed with salt water containing H_2S and 250-300 ppm CO_2. The fatigue performance was lowered slightly with the addition of Diesel fuel to this environment. Figure 3 shows the effect of a hydrocarbon phase in the carbon dioxide and brine system. Diesel fuel did not seem to affect the corrosion fatigue performance in this environment at all. Overall, the Diesel fuel seems to have had no significant effect.

INHIBITOR EVALUATION

Procedures for Inhibitor Tests

The procedures that were followed in the inhibitor evaluation tests were as follows:

(1) The Diesel fuel was deaerated by bubbling nitrogen through the Diesel fuel container for several hours (overnight).
(2) The salt solution was saturated with gases of interest (overnight).
(3) The Diesel fuel was introduced into the corrosion fatigue box under a blanket of nitrogen gas.
(4) Saturated salt solution was introduced into the box displacing Diesel fuel to the top. A positive gas pressure on the box prevented air contamination of the system.
(5) The solution was stirred in order to obtain a good emulsion (2 minutes). Inhibitor was added while mixing the solution.
(6) The stressing cycles were started. Whenever dealing with an oil-soluble inhibitor, the inhibitor was added after the (3) step and the mixture was stirred for 3-4 minutes. In this case the salt water slowly displaces Diesel fuel to the top such that the sample was coated with a

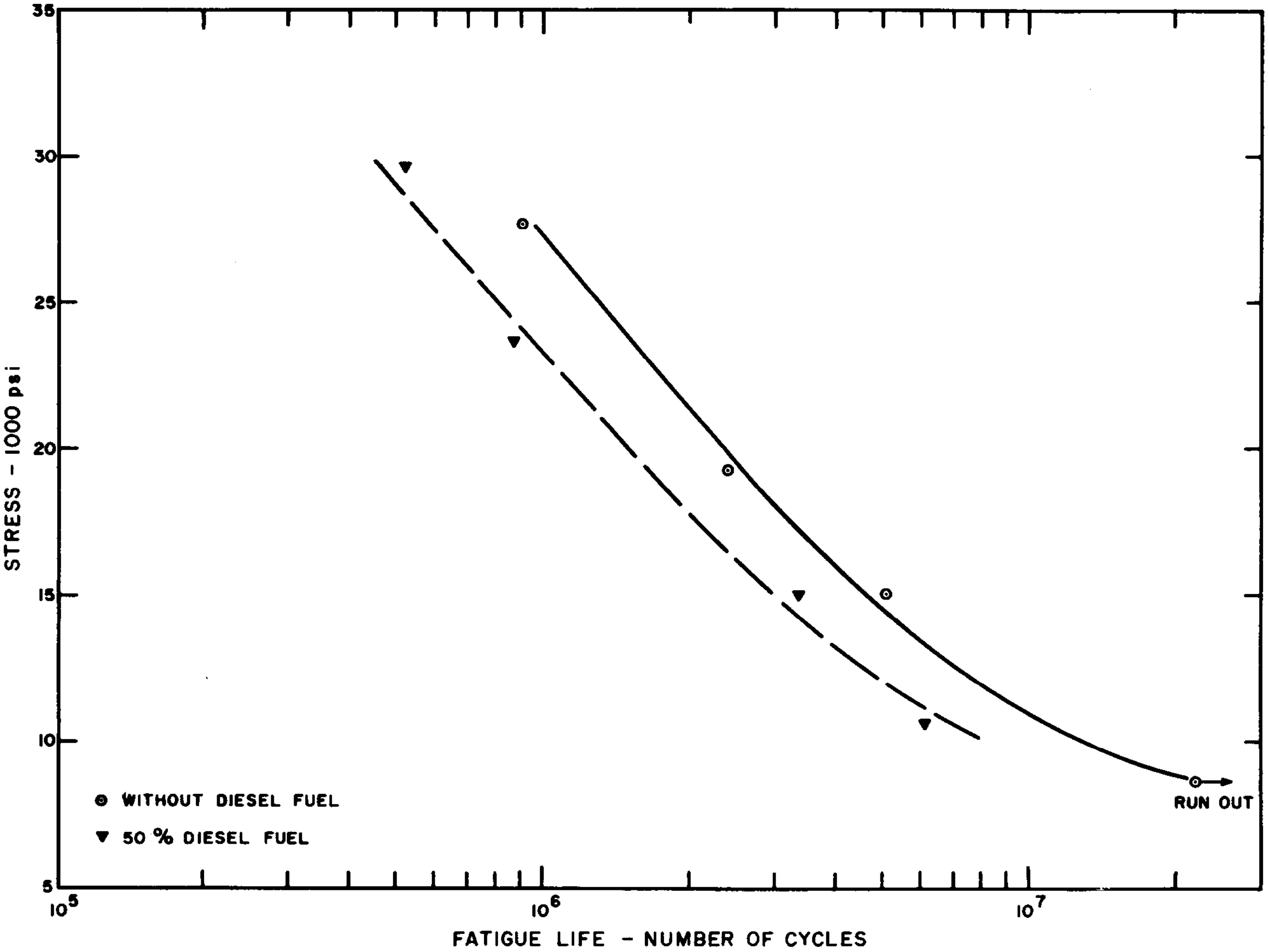


FIG. 4 CORROSION FATIGUE TESTS IN SALT WATER CONTAINING 70 ppm H_2S AND 240 ppm CO_2

thin film of Diesel fuel and inhibitor before corrosion fatigue commenced. In the case of water-soluble inhibitors where the inhibitor was added during step (5), the sample was coated only with a thin film of Diesel fuel.

The inhibitor concentrations shown in the tables are not the concentrations of the active ingredients but of the inhibitors in the commercially available condition.

TEST RESULTS

The results of tests in the inhibited system are shown in Tables 3 and 4. Corrosion protection measurements are also shown in Tables 3 and 4.

Table 3

Inhibitor Evaluation in Mixture of Salt Solution and Diesel Fuel

Containing H_2S (70 ppm) - CO_2 (240 ppm)

Bending Stress = 27,690 psi.
Corrosion fatigue life without inhibitor = 5.95×10^5 cycles.

Inhibitor	Conc. ppm	Ave. Inhibited Corrosion Fatigue Life	$R = \frac{\text{Inhibit.}}{\text{Uninhib.}}$	Solubility of Inhibitor	% Protection (Corrosion)**
A	100	1.5×10^6	2.5	Water sol.	71%
B	50	0.28×10^6	0.5	Oil sol. Water disp.	25%
C	50	2.55×10^6 1 N.F.*	1-4.9	Oil sol. Water disp.	29%
D	50	5.5×10^6 2 N.F.*	1.6-9.2	Water sol.	80%
E	50	0.79×10^6	1.3	Oil sol. Water disp.	-3%
F	50	3.5×10^6 1 N.F.*	1.2-5.1	Water sol.	25%
G	50	1.37×10^6	2.3	Water sol.	50%
O	50	7.37×10^6 2 N.F.*	6.9-12.3	Water sol.	95%

* N.F. = sample did not fail up to $\approx 10^7$ cycles.

** Based on corrosion coupon rates.

Table 4

Inhibitor Evaluation in Mixture of Salt Solution and Diesel Fuel

Saturated with CO_2

Bending stress = 31,590 psi.
Corrosion fatigue life without inhibitor = 1.25 x 10^6 cycles.
All inhibitors tested at 50 ppm concentration.

Inhibitor	Average Corrosion Fatigue Life (cycles)	$R = \frac{\text{Inhibit.}}{\text{Uninhib.}}$	Solubility	% Protection (Corrosion)**
H	5.59 x 10^6	4.5	Water sol.	21
I	2.08 x 10^6	1.7	Water sol.	24
J	2.86 x 10^6	2.3	Oil sol.	22
K	2.26 x 10^6	1.8	Water sol.	38
L	4.03 x 10^6	3.2	Oil sol.	82
M	2.63 x 10^6 (1 N.F.)*	2.1-3.7	Oil sol.	30
N	4.38 x 10^6 (2 N.F.)*	3.5-5.6	Water sol.	72

*** N.F. = sample did not fail up to 10^7 cycles.**

**** Corrosion rate data from corrosion coupons.**

The corrosion rates were measured using corrosion coupons suspended in the system for the duration of the test. The per cent protection was then obtained by comparing the inhibited corrosion rate data with rates calculated (extrapolated) from a curve for a "no-inhibitor" environment at the same exposure duration.

The ratio (R) of corrosion fatigue improvement was obtained by calculating the ratio of the average life of four fatigue specimens in an uninhibited environment to the average life of four fatigue specimens at the same bending stress in the same environment but with an inhibitor. This stress level was 27,690 psi for the ($H_2S + CO_2$) system and 31,590 psi for the CO_2 system. If the corrosion fatigue specimen did not fail up to 10^7 cycles, it was designated as N.F. For calculation purposes, the effective life of these N.F. samples was considered to be 10^7 cycles. The four specimens that were used in each test consisted of two oil quenched (B1 - Table 2) and two water quenched and tempered (B4 - Table 2). As noted from Table 2, these two different heat treatments produced equivalent levels of strength. The hardness of these samples was in the 14-18 Rockwell C range.

As noted from Tables 3 and 4, there were significant variations in the effectiveness of these different organic inhibitors on the corrosion fatigue performance of the steel in the "inhibited" environments.

EFFECT OF INHIBITOR CONCENTRATION

The effect of inhibitor concentration on the improvement ratio at a fixed fatigue stress was determined in both the carbon dioxide brine and the hydrogen sulfide-carbon dioxide brine systems. In these tests four specimens, two of steel B1 and two of steel B4, were used. Figure 5 shows the results of tests completed to date in both systems. It is evident from the limited data obtained thus far that the improvement in corrosion fatigue life depends on the inhibitor composition and the environment. This can be seen from the variation in effectiveness with different inhibitors in Fig. 5. At low concentrations (less than 20-50 ppm) none of the inhibitors yet tested showed any significant effectiveness. At concentrations between 50 ppm and 100 ppm some inhibitors (G and F) begin to show drastic improvements in effectiveness. One of these (inhibitor G) reached maximum effectiveness by our test scheme ($R=16$) at a concentration of 200 ppm. The concentration at which such improvement begins to develop differs for different inhibitors. One inhibitor—and there will probably be others—produced no significant corrosion fatigue improvement even at a 240 ppm concentration.

EFFECT OF STRESS ON THE INHIBITED ENVIRONMENT

The above tests were run at a fixed stress with variable inhibitor concentrations. Additional tests were run at fixed concentrations of inhibitor. The magnitude of stress in the inhibited environment was changed so as to obtain the S-N curves shown in Figs. 6, 7 and 8. These tests were run with inhibitors and at concentrations which had demonstrated some effectiveness in the fixed stress tests. Corrosion coupons inserted in the CO_2 + brine system showed a 70-75 per cent protection at 50 ppm concentration of inhibitor N. Similar corrosion rate data in the $H_2S + CO_2$ + brine system showed 70-75 per cent protection at 100 ppm of inhibitor A. In the case of inhibitor N in the CO_2 system the effectiveness of the inhibitor was almost constant with the change in stress level. This is also confirmed by the data in Fig. 7. This data was obtained using specimens of higher strength (steel B2) so the S-N curve in the inhibited system was at a higher level than that in Fig. 7. The corrosion rate data showed 40-60 per cent protection at the 200 ppm concentration of the inhibitor used in these tests. On the other hand, the effectiveness of inhibitor A in the H_2S-CO_2 system increased with decreasing stress level (Fig. 8).

DISCUSSION

There does not seem to be any accepted theory for the exact mechanism by which the organic inhibitors function. It is proposed[1,4] that organic inhibitors are effective by virtue of their attachment to the metal surface. This adherence is due to the combined action of physical and chemical adsorption. Whether the adsorption is initially chemisorption or physical adsorption followed by chemisorption has not been clearly resolved. According to Bergman's literature summary[2] there is adequate data to show that a direct relationship exists between the bond strength of the chemisorbed layer and the effectiveness of the inhibitors.

Bergman has proposed a theory[2] based on the

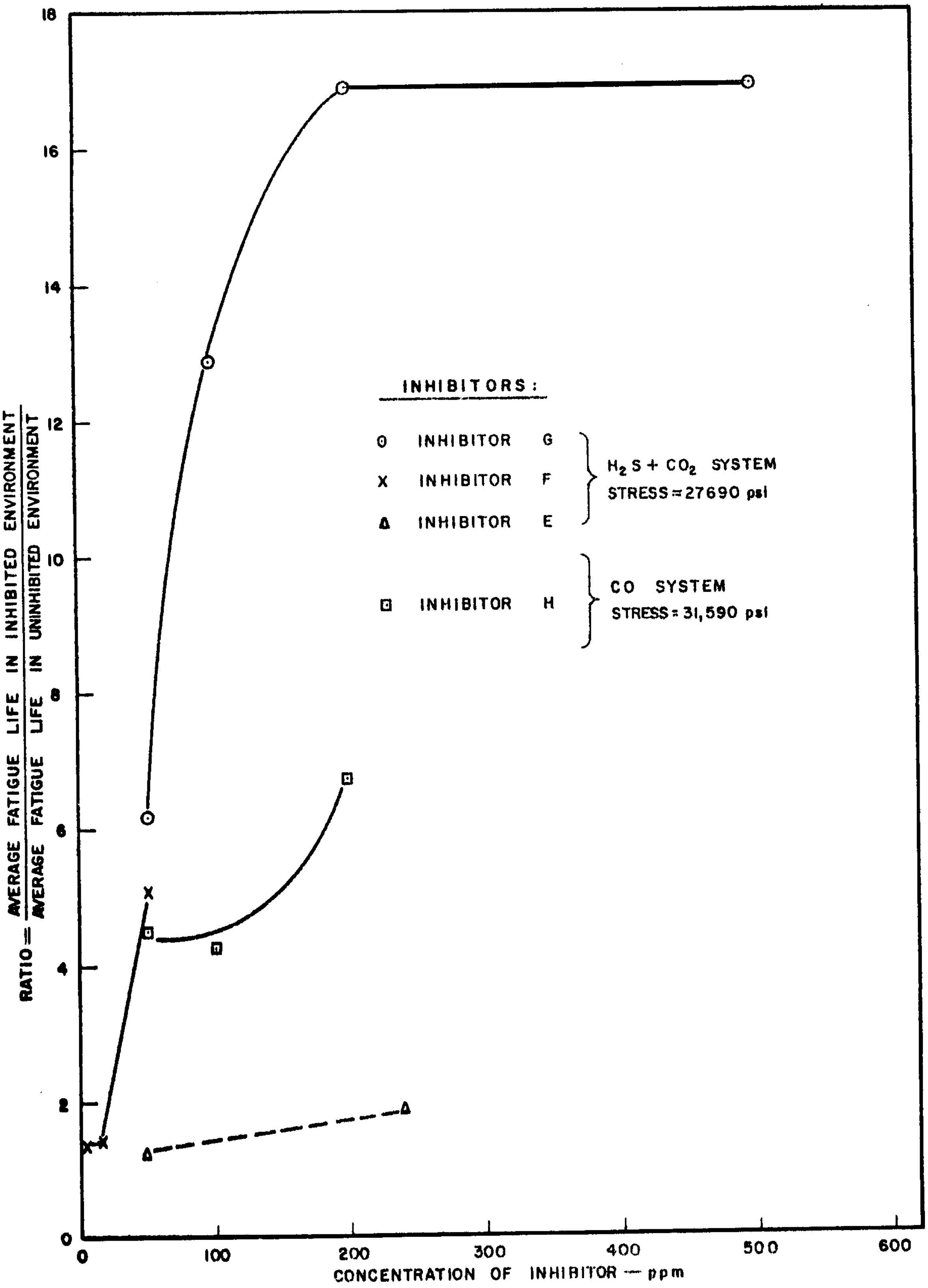

RATIO = AVERAGE FATIGUE LIFE IN INHIBITED ENVIRONMENT / AVERAGE FATIGUE LIFE IN UNINHIBITED ENVIRONMENT
0
2
4
6
8
10
12
14
16
18
0
100
200
300
400
500
600
CONCENTRATION OF INHIBITOR — ppm
INHIBITORS:
○ INHIBITOR G
X INHIBITOR F
Δ INHIBITOR E
H₂S + CO₂ SYSTEM
STRESS = 27690 psi
▣ INHIBITOR H
CO SYSTEM
STRESS = 31,590 psi

FIGURE 5

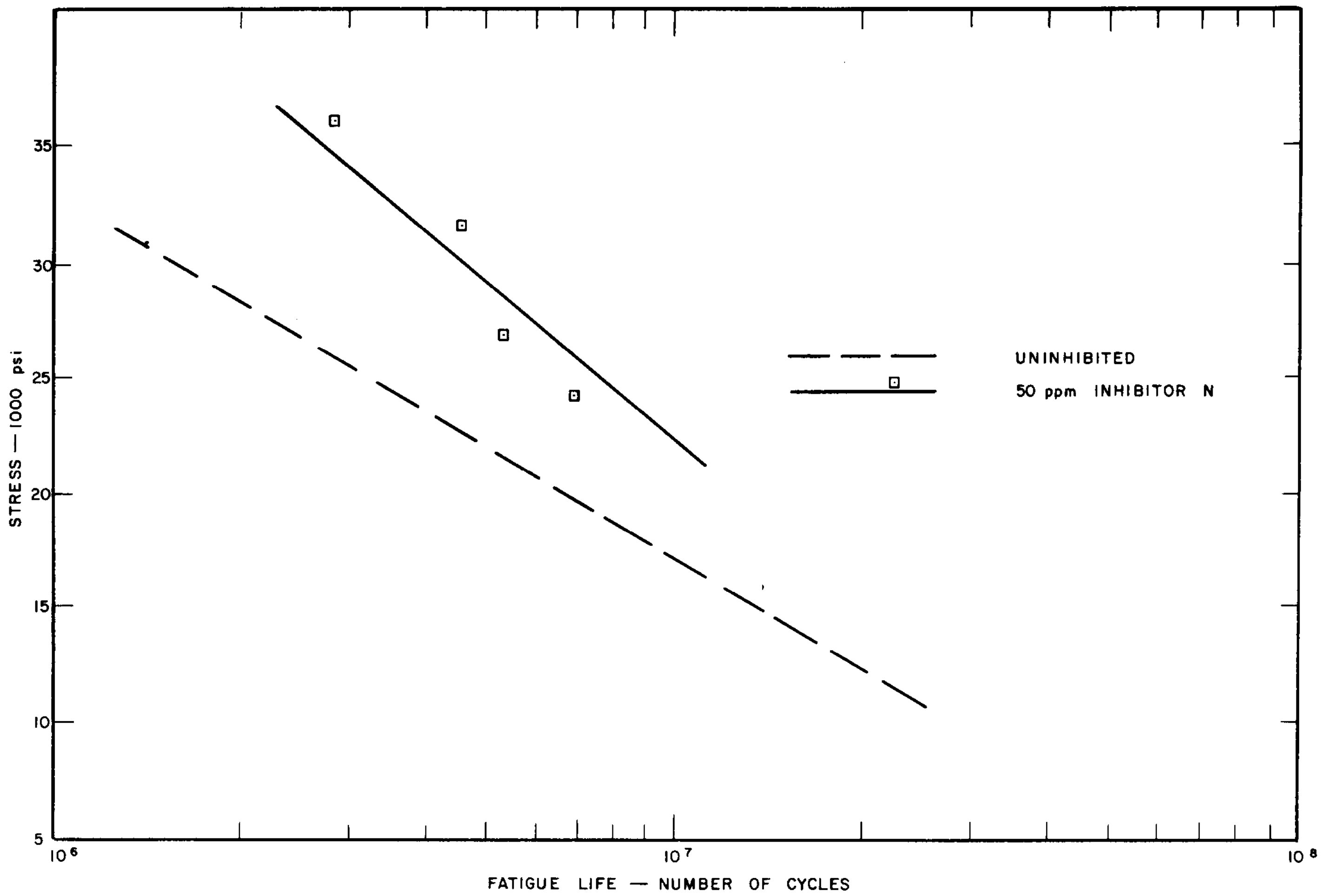


FIGURE 6
CORROSION FATIGUE DATA BRINE + DIESEL FUEL + CO_2

bond strength of the inhibitor molecule, to explain the protective action of organic inhibitors in oil and gas wells. This theory postulates that the protective action can be thought of in terms of a "sandwich" mechanism. The bottom part of the sandwich is the bond between the polar end of the molecule and the metal surface. The center portion of the sandwich is the nonpolar end of the molecule and its contribution toward protection is the degree to which this portion can cover or wet the surface. The degree of coverage, of course, depends on the orientation of the long-chain portion of the molecule. The outside layer of the protective sandwich is the hydrophobic layer of oil attached to the long hydrocarbon tail of the inhibitor. This last layer is believed to contribute to the general protection by forming a barrier to both the outward diffusion of Fe and the inward diffusion of the corrodents.

It is interesting to discuss test results in the light of the above protection mechanism. It should be noted here that while any amount of protection would represent some kind of improvement from the standpoint of corrosion rate alone, this does not hold true in the case of corrosion fatigue. Any unprotected area would serve as a nucleation site for a corrosion fatigue crack regardless of the degree of protection provided for the neighboring areas. While this type of inhibition shows partial protection from the standpoint of material loss it does not provide any improvement in corrosion fatigue performance.

The improvement ratio in Fig. 6 changed very little for low concentrations of inhibitors.

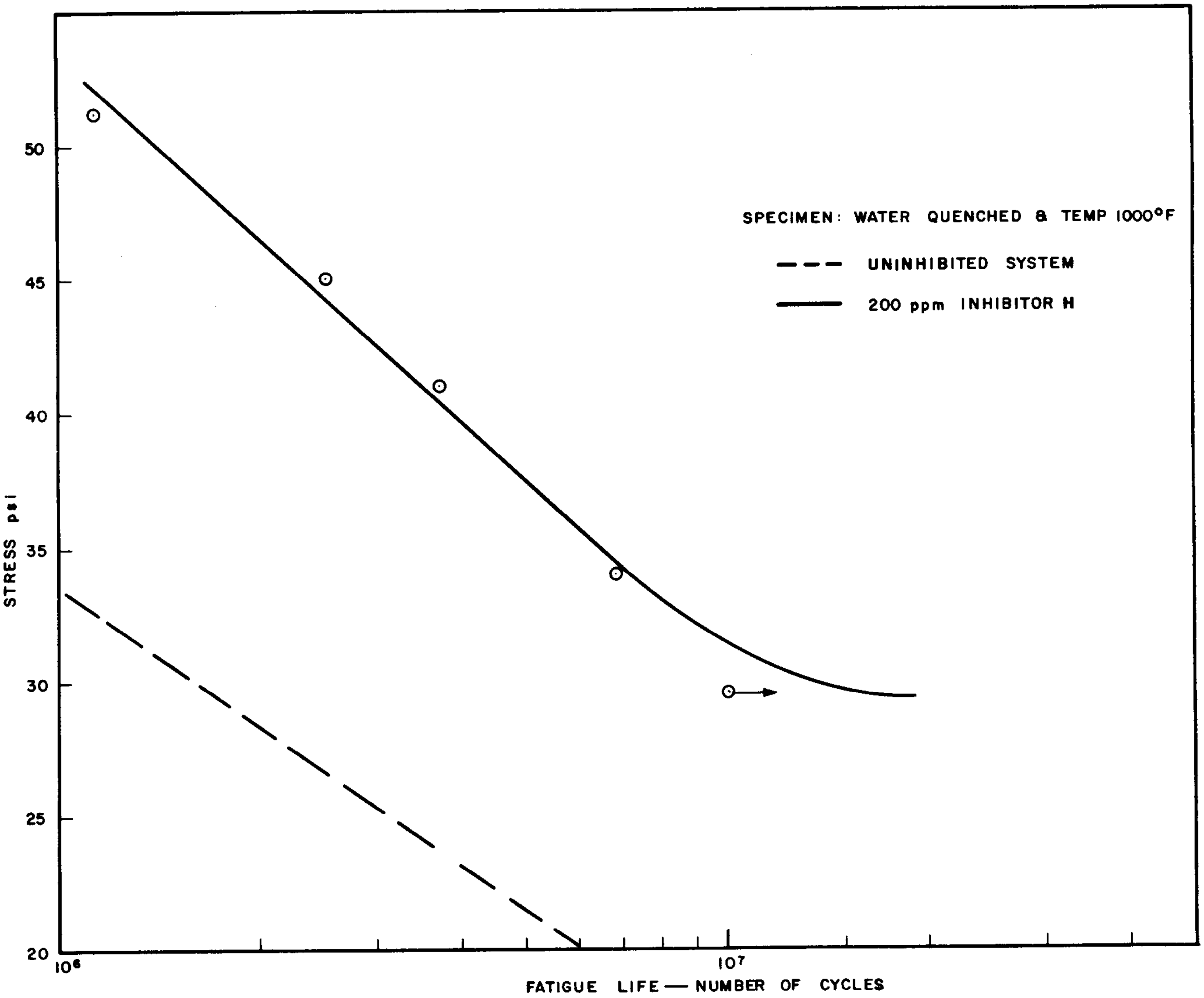


FIGURE 7
CORROSION FATIGUE DATA BRINE + DIESEL FUEL + CO_2

As the inhibitor concentration was increased, however, some point was reached above which the inhibitor begins to provide protection. Above this concentration the improvement ratio seems to increase rapidly and then reaches a plateau at almost complete protection. We normally fail to register this type of information with our corrosion coupon data, perhaps because of insufficient accuracy in our corrosion rate measurement technique.

These points can be illustrated by Fig. 9 which shows the appearance of corrosion fatigue on coupons from the inhibited $H_2S + CO_2 +$ brine + Diesel fuel system. Here the transition from partial to full protection can be seen as a function of inhibitor concentration. The dark spots on the specimens represent areas where there seemed to be discontinuities in the inhibitor film. Actually, all of these coupons should be "covered" with inhibitor, but the environment is able to penetrate the protective layer and cause some amount of underfilm corrosion. These spots appeared as small dots at first and gradually spread as more underfilm corrosion took place. All of the inhibitors tested provided inhibitor film coverage for the specimens. All were not equally effective in preventing corrosion fatigue.

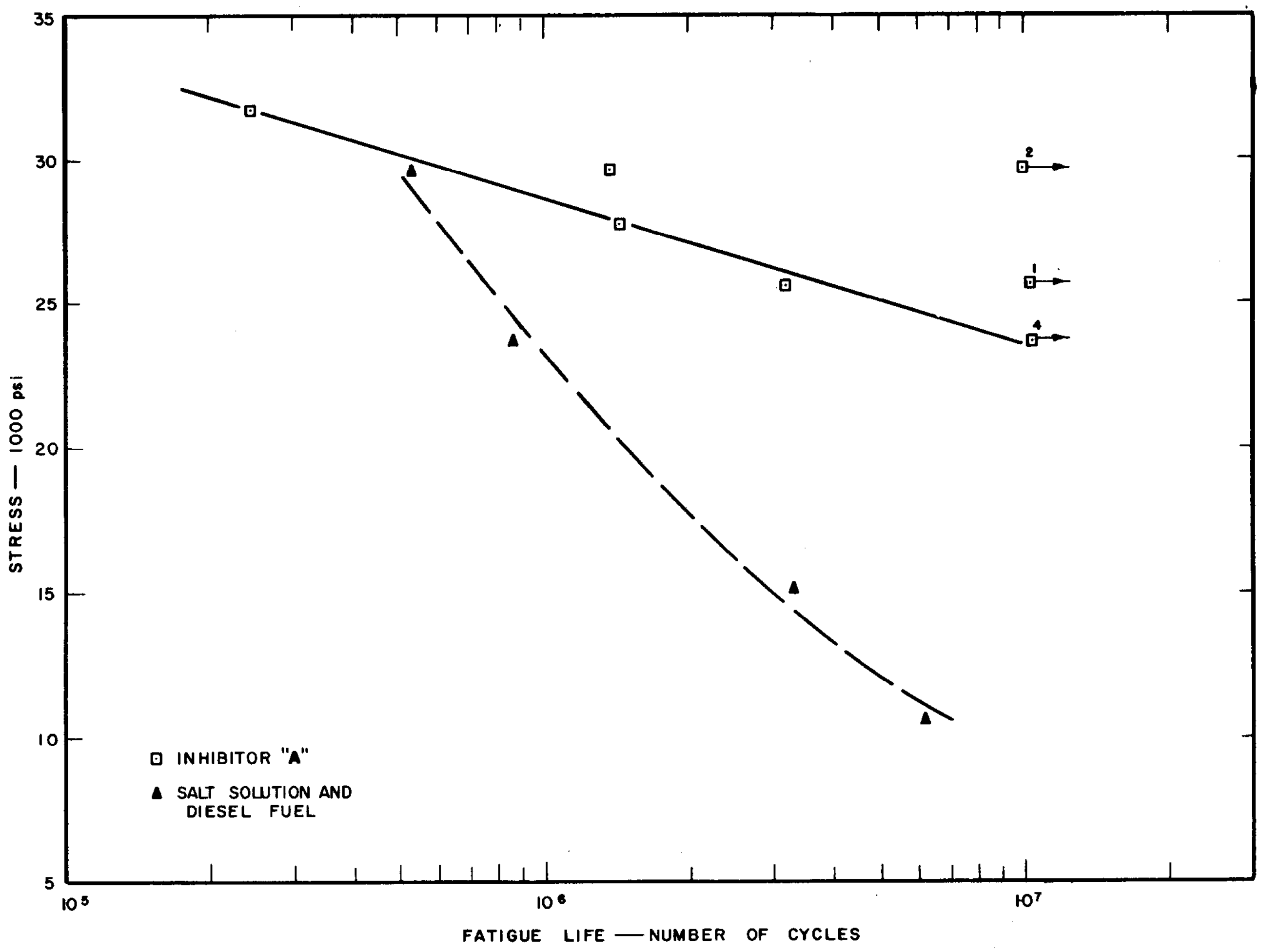
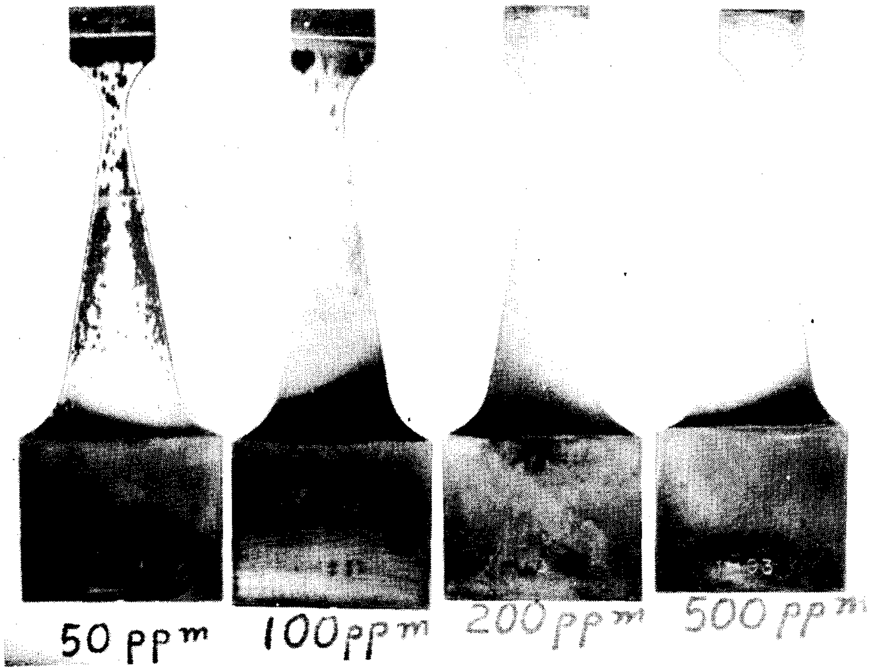


FIG. 8 CORROSION FATIGUE TESTS IN A MIXTURE OF 50 % DIESEL FUEL AND 50 % SALT SOLUTION CONTAINING 70 ppm H_2S, 240 ppm CO_2, AND 100ppm OF INHIBITOR A.

At low concentrations of inhibitor, corrosion fatigue failures seemed to occur as a result of corrosion at spots where there was a break in the inhibitor film. At high concentrations the failures occurred at spots where there was an indication of underfilm corrosion. It is therefore reasonable to propose that the critical concentration of inhibitor in corrosion fatigue (concentration at which R rapidly increases) is the point at which the second layer—or maybe the third layer—in the "sandwich theory" provides complete coverage. The corrosion fatigue process would then depend upon the diffusion of corrodent through the outer layers of the "sandwich." The corrosion fatigue performance increases rapidly as the third layer becomes less permeable through an increase in inhibitor concentration. On the other hand, acceptably high levels of corrosion protection are probably achieved with only partial second and third layer coverage.

It may be noted here that all of the concentrations for effective corrosion fatigue protection are very high compared with the inhibitor concentration that oilfield equipment normally receives in practice. With this in mind it is interesting to note that the corrosion fatigue behavior of steel in the inhibited environment, in the absence of complete inhibition, would vary with the magnitude of applied stress in a manner shown in Figs. 7, 8 and 9. The shape of the S-N curve depends on the nature of corrosive environment. The increase in corrosion fatigue life with the lowering of applied stresses may be attributed to the following factor. The inhibited environment at inhibitor concentrations below



Appearance of Inhibitor O Coated Corrosion Fatigue Specimens at Various Concentrations of Inhibitor After Test in H_2S+CO_2 System.

FIGURE 9

complete inhibition could be thought of as the uninhibited environment of somewhat lower corrosivity. For a $H_2S + CO_2$ system the corrosion rate is high initially and drops rapidly for four or five days. The inhibited corrosion fatigue life reacts accordingly, keeping in mind that N is a function of time. The corrosion rate in the CO_2 system on the other hand drops at a much slower rate. The corrosion fatigue curve in this environment behaves similarly.

CONCLUSIONS

The inhibitor concentration required to give significant protection to steel under corrosion fatigue conditions is much higher than that for corrosion control. This is due to the fact that corrosion fatigue cracks are initiated at incompletely protected spots on the material regardless of the degree of protection received by neighboring areas. Therefore, complete coverage and protection by all three parts of the inhibitor sandwich is required before any considerable improvement in corrosion fatigue life is observed. Due to this fact it would be very hard to determine the effectiveness of a corrosion fatigue inhibitor from the data obtained by corrosion rate measurements. The corrosion fatigue curves in the inhibited environments, at concentrations below the level of complete protection, vary according to the nature of the corrosion process in that environment.

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