CORROSION FATIGUE OF MILD STEEL

By

James M. Cairney, B.Sc., A.R.T.C.

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INTRODUCTION.

INTRODUCTION.

Although it is some forty years since Haigh(1) first recognised and investigated the phenomenon of corrosion fatigue, and although much experimental effort has since been devoted to its study, no quantitative theory of corrosion fatigue has yet been produced. Such a theory would permit the accurate estimation of the corrosion fatigue endurance of a component by reference to the properties of the component material and to the chemical and physical nature of the component environment. Until such a theory has been established, this subject must continue to repay experimental study and it was with the hope that some extension of knowledge would result that the author undertook the research described in this thesis.

A study of corrosion fatigue must properly be based on an understanding of the electrochemical theory of corrosion. The author has therefore included a brief review of the salient features of this theory in the survey of published work contained in the following chapters. This survey attempts a critical analysis of the phenomenon of corrosion fatigue based on the several researches which have been carried out during the past forty years. Additionally, the survey covers the work done on the inhibition of corrosion fatigue in aqueous environments by the use of chemical additions.

The experimental programme which formed the basis of the present research was selected with particular reference to a practical aspect of marine engineering. Occasional, but costly corrosion fatigue failures of water-cooled diesel engine piston rods have occurred in marine engines. Such failures have been attributed to undetected infiltration of sea-water into the fresh-water cooling system, with the resultant chloride concentration rendering ineffective the corrosion inhibitors normally present in the cooling system. Thus, the material, the environments and the test conditions chosen were such as to allow an assessment to be made of the efficacy of various inhibitors under corrosion fatigue conditions akin to those found in service.

In discussing the experimental results, the author has sought to reconcile the quantitative graphical relationships obtained with the qualitative metallographic evidence, on the basis of the electrochemical theory of corrosion and the established characteristics of the fatigue of metals. Thus, it has been shown that a change in the mechanism of failure at a particular stress level is consequent upon a limiting value for the effective stress concentration factor associated with a corrosion fatigue pit in mild steel. It has also been concluded that the rate of propagation of a corrosion fatigue crack at a given stress level is dependent upon the electrical conductivity of the corrosive medium. A theoretical explanation of this, based on the electrochemical energy equation for the corrosion process, has been developed.

Although a fully quantitative theory of corrosion fatigue is still required, these conclusions in particular should serve to form a more rational basis for the study of the phenomenon than was formerly available.

PART I.

SURVEY OF PUBLISHED WORK.

CHAPTER I.

THE CORROSION OF STEEL IN AQUEOUS MEDIA.

Corrosion may be defined as the destruction of a metal by reaction with its environment. Where this environment is solid or gaseous the reaction is, in general, a purely chemical one but where aqueous media are involved then an electrochemical reaction can be shown to account for almost all of the corrosion. An electrochemical reaction in this context is one where separate anodic and cathodic areas are involved, and where detectable electric currents flow within the metal between those areas.

Conclusive evidence that such electric currents flow, and that they account quantitatively for the corrosion product, has been produced by Hoar and Evans(2) in the case of a steel plate partially immersed in a solution of potassium chloride. Thornhill and Evans(3) showed that in the case of iron wetted with sodium bicarbonate solution the corrosion was accounted for by the current flowing between a scratch line as anode and the remainder of the plate as cathode. The electrochemical nature of corrosion in aqueous media is thus clearly established.

The existence of anodic and cathodic areas on a single specimen of metal having been demonstrated, it is of interest to consider the sources of these potential differences. Mears and Brown(4) have examined these sources and have listed some seventeen possible factors. Of these, the following are of particular interest in this investigation:

(1) The presence of impurities in the metal.

(2) Local scratches or abrasions on the metal.

(3) Differential strain within the metal.

(4) Differential concentration of the corroding solution.

(5) Differential aeration of the solution.

In any particular instance, one or more of these factors may determine the location and extent of corrosion.

In the case of a short circuited simple cell consisting of two different metallic electrodes immersed in an electrolyte, polarisation at the anode and/or cathode may stifle the production of an electric current. Similarly, with the corrosion of a single material immersed in an aqueous medium polarisation at anodic and/or cathodic areas serves to reduce the corrosion rate by producing a back e.m.f. which opposes the original potential difference.

Warner(5) has expressed the limiting corrosion rate for a reaction by setting the energy decrease in the process equal to the sum of the energies dissipated in the various parts of the electrochemical system. Thus, converting the energies to potentials.

$$E_r = E'_a + E'_c + E'_{IRi} + E'_{IRe}$$

where, E_r = reversible electromotive force of the couple

E'_a = total polarisation at anode areas.

E'_c = total polarisation at cathode areas.

$E'_{IRi} = IRi$ = Current flowing x resistance of electrolyte between cathode and anode areas.

E'_{IRi} = IRe = Current flowing x resistance of metal between cathode and anode areas.

Since the factors on the right hand side of the above expression are functions of current density, it follows that an increase in any one of them will reduce the current flowing and hence the corrosion rate. The factors E'_{IRe} is generally negligible due to the high conductivity of the metal, and the factor E'_{IRi} diminishes rapidly as the salt content of the aqueous medium is increased. Thus the corrosion rate is generally dependent on the degree of polarisation at anode and/or cathode. It is upon the increase of polarisation at either cathode or anode that many methods of corrosion control depend.

In the case of iron subjected to the action of aerated water, the reactions at anodic and cathodic areas are as follows.

At anodic areas. $Fe \rightarrow Fe^{++} + 2e^-$ .... (1)

At cathodic areas. $H^+ \rightarrow \frac{1}{2}H_2 - e^-$ .... (2)

$2H^+ + \frac{1}{2}O_2 \rightarrow H_2O - 2e^-$ .... (3)

Reaction (2) is very slow in neutral or alkaline media and accounts for a very small proportion of the observed corrosion. The remainder is due to the oxygen consuming reaction (3).

The composition and physical nature of the rust formed on iron has been found to vary with experimental conditions. Cox and Roetheli(6) have demonstrated that as the concentration of dissolved oxygen is increased, the corrosion rate at first rises, the product being largely granular black magnetite. At higher oxygen concentrations, however, the formation of gelatinous ferric hydroxide can be observed. The protective nature of this deposit retards the corrosion rate. The changes in free energy involved in the reactions which produce magnetite (Fe_3O_4) and ferric hydroxide [$Fe(OH)_3$] from iron immersed in distilled water and saturated with air are both of the order of minus 80,000 calories per gram molecule of iron. An increase in osygen concentration favours the production of $Fe(OH)_3$ while a decrease favours the formation of magnetite. In practice, under conditions of maximum aeration at atmospheric pressure, a partially hydrated ferric oxide, $Fe_2O_3.xH_2O$ (where $x < 3$), seems to be the most stable end product of corrosion.

The addition of sodium chloride to aerated distilled water greatly accelerates the corrosion of iron. By increasing the conductivity of the medium, the chloride ions allow the passage of current between more remote anodic and cathodic areas. In addition, the rust formed by the interaction of anodic and cathodic products tends to deposit further away from the iron surface, thus lessening its protective action. According to Uhlig(7) the increase in corrosion rate with salt concentration reaches a maximum about 2% sodium chloride by weight, further addition of chloride reducing corrosion due to the accompanying decrease in oxygen solubility.

Variation in the temperature of the aqueous medium is reflected by a change in the rate of corrosion. With rising temperature, the dissolved oxygen diffuses more readily towards the metal surface and so accelerates the corrosion reaction. This effect, however, is opposed by the decreased oxygen solubility at higher temperatures. Friend(8) has shown that this results in a maximum corrosion rate around 80°C.

Whitman, Russell, and Altieri(9) investigated the influence of pH on the corrosion of mild steel. They showed that at 22°C, the corrosion rate was unaffected by change of pH within the range pH = 4.0 to pH = 9.5. This can be explained by considering that the metal surface is always in contact with a saturated solution of ferrous hydroxide of pH = 9.5 which is unaffected by changes in pH within the range stated. In solutions of pH above 9.5, the corrosion rate is reduced by stifling of the cathodic reaction, while at a pH less than 4.0, attack by hydrogen evolution commences and the rate of corrosion rises sharply.

Another important variable affecting corrosion is the rate of flow of medium past the metal surface. Roetheli and Brown(10) investigated the influence of velocity on the corrosion rate of steel. They found a pronounced maximum damage at a specific velocity and explained this as the result of two opposing tendencies. Initially, a rise in velocity reduces the thickness of the stagnant film of liquid adhering to the metal surface. The increased diffusion of oxygen results in increased corrosion. Further increase of velocity, however, produces turbulence which destroys the stagnant film altogether and by virtue of the greatly increased availability of oxygen promotes the formation of gelatinous ferric hydroxide. The protective nature of this deposit reduces the corrosion rate.

It may be seen from the foregoing, that oxygen plays a principal role in the corrosion of ferrous materials in aqueous media. Any variation in experimental conditions which influences the amount of dissolved oxygen available to the metal-liquid interface will necessarily affect the degree of corrosion and the nature of the corrosion product.

CHAPTER II.

CHARACTERISTICS OF CORROSION FATIGUE.

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Definition.

The phenomenon of corrosion fatigue, first experimentally investigated by Haigh(1) is a clearly defined one. He states "Where the surface of the specimen has been appreciably roughened by corrosion prior to fatigue testing, the endurance has naturally been reduced; but .... this effect is generally small in comparison with the reduction that occurs when the surface is moistened with the reagent during the test." This statement clearly distinguishes the separate actions of corrosion and fatigue from their conjoint action, and all subsequent research has confirmed this early view.

Gough(11) defines corrosion fatigue as "The behaviour of metals subjected to cyclical stresses while exposed to an environment of an oxidising nature".

The phenomenon is defined by Gould(12) in these terms - "In general, fatigue combined with corrosion behaves as if it were an intensified form of fatigue, and the severity of the action is dependent upon the range and frequency of the stress, the intensity of the corroding medium, and the time taken."

Appearance of fracture.

Failure by corrosion fatigue produces a fracture which is quasi-brittle as in simple fatigue but which exhibits a characteristic discolouration. This discoloration is most marked at the nucleus of the crack becoming less pronounced with increasing distance from it. The

Simple Fatigue

Corrosion Fatigue

PLATE 1. APPEARANCE OF FATIGUE FRACTURE FACES.

gradation in colour is a reflection of the decrease, with increasing penetration, of the time for which the crack surfaces have been exposed to corrosion.

It is also characteristic of corrosion fatigue, that failure results from a number of cracks which join up to produce a serrated fracture. This is in contrast to simple fatigue failure where, most commonly, final fracture results from the extension of a single crack, although there may be other cracks in the vicinity. The difference in appearance of the two types of fracture is illustrated in Plate I which shows two laboratory specimens produced by the author.

Stress-Endurance ($^S/_N$) Curve.

The absence of a "safe range of stress" where corrosion fatigue conditions prevail is the most important practical consideration revealed by the extensive experimental work published over the last forty years. Whereas in the simple fatigue of ferrous metals, the S/N curve tends to an asymptote of stress below which specimen life may be anticipated as infinite, corrosion fatigue results lie on a curve showing no such asymptote. This is true even for mildly corrosive conditions, and means that in practice a component may eventually fail, even though only subjected to a small range of cyclic stress, if in contact with a corrosive medium. It is clear then that the term "corrosion fatigue limit" cannot be justified and the term "endurance limit" must be related to a specified number of stress reversals.

A great many workers in this field present their results in the form of S/N curves, or some logarithmic modification of these. Since, however, many experimental factors are involved it becomes difficult and even misleading to compare directly the results of different workers. The influence of such experimental factors is discussed in detail in Chapter 3.

Microstructure:

Microscopical examination of sections containing corrosion fatigue cracks shows that their path is almost exclusively transcrystalline in ferrous materials. In the excellent experimental work of McAdam and Geil(13) on pit formation, it is established beyond doubt that the cracks spread from the extension of sharp fissures which develop on the specimen surface. These fissures have their origin in heimspherical pits of the type associated with stressless corrosion. The development of these crevices from rounded-pits is clearly shown by McAdam and Geil to be dependent upon the range of cyclic stress involved. The puzzling feature of the process is that cyclic stress may have a considerable effect upon the size and form of a few pits while having little effect upon the remainder. It was not found possible by these workers to establish a criterion of failure from the form and type of pitting.

CHAPTER III.

FACTORS INFLUENCING THE SEVERITY OF CORROSION FATIGUE.

Metal Composition.

It has been established that alterations in the composition of an alloy will improve its resistance to corrosion fatigue only if these alterations improve its normal corrosion resistance. McAdam(14) in an extensive investigation of the resistance of carbon and low alloy steels found that despite the great range of mechanical properties involved, compositional changes had little influence on the corrosion fatigue life of these materials. It is not until corrosion resistant alloys (e.g. 18% Cr/ 8% Ni) are considered, that any major improvement is found.

Heat Treatment.

Little change in corrosion fatigue resistance of low alloy steel can be produced by any process of heat treatment. Indeed, annealed specimens(14) have been found to show slightly greater endurances than hardened material. This agrees with the general proposition that it is the corrosion properties of the material that determine its resistance to corrosion fatigue.

Surface Condition.

Gould and Evans(15) have demonstrated that a considerable improvement in the endurance of steel specimens under corrosion fatigue conditions in dilute sulphuric acid and in seawater may be produced by shot peening. At a stress range of ± 10 T/in^2 in sea-water, the specimen life increased from 0.8 x 10^6 reversals in the unpeened condition to

7×10^6 reversals when peened. They suggest that peening, by inducing residual compressive stresses in the surface layers of the specimen, retards the development of the crevice type cracks from the original saucer-shaped cavities produced by corrosion. To the author, however, it seems likely that potential differences existing between areas of a steel surface will be reduced by the extensive cold-work involved in shot-peening. Thus, the probability of corrosion starting would be lessened and the onset of pitting delayed.

Tests of shot-peened specimens were also carried out by Gould and Evans in the presence of alkaline inhibitors where these were present in a "dangerous" concentration, insufficient to ensure complete protection. Under these conditions, peened specimens displayed a <u>shorter</u> fatigue life than the unpeened ones. They consider that this results from the internal conditions in the peened specimens being more suitable for rapid crack propagation than in unpeened ones. Certainly the residual compressive stresses induced on the metal surface by peening will be accompanied by residual tensile stresses within the body of the specimen and it is understandable that a crack will advance more easily through a material containing such stresses.

The effect of protective coatings on the corrosion fatigue resistance of steel in salt spray was investigated by Sapwith and Gough(16). They found that galvanising and sherardising increased specimen life considerably due to the cathodic protection conferred by the zinc coating. A high degree of protection was also conferred by a sprayed aluminium coating which had been enamelled, and to a lesser extent by cadmium plating and phosphating.

Applied stress system.

The majority of laboratory experiments have been conducted under conditions of cyclic tension-compression. In comparative tests using direct push-pull loading in one case and rotating beam specimens in the other, Gough and Sopwith(17) found considerable differences in endurance. In these tests, carried out in salt spray on six ferrous materials, rotating beam specimens displayed, in general, greater endurances at comparative stresses than specimens loaded in direct push-pull. Only in two cases, at low stresses, did the reverse hold.

Gould(18), however, carrying out similar tests on mild steel under conditions of total immersion, found that at normal working stresses specimens subjected to push-pull loading displayed endurances of approximately five times that of comparative beam specimens. He explains this as resulting from the greater intensity of corrosion currents flowing in the case of rotating beam specimens. During the tensional half-cycle of push-pull loading, all the anodic areas on the specimen are simultaneously subjected to maximum strain. Thus the ratio of anode to cathode area is lower than in the case of rotating-beam specimens where only a fraction of the anodic areas are correspondingly exposed at a given instant. Under conditions of partial cathodic control this difference in ratio will produce a corresponding difference in corrosion intensity.

Specimen size.

The possible existence of a "scale effect" in corrosion fatigue has not been fully investigated but McAdam(19) has shown that variation of specimen diameter within the range 0.5 to 2.3 inches had no significant effect on the endurances recorded when specimens of a heat-treated low alloy steel were subjected to fatigue in the presence of tap-water. This matter is one of some importance where laboratory results are to be related to practical conditions.

Mean Stress.

Gould(18) investigated the influence of mean stress on specimen endurance, and found that within the range 0 to 8 Tons/in^2 the superimposition of a tensile stress upon reversed stress caused no serious deterioration of behaviour.

Gough and Sopwith(20) studied the effect of a much wider range of mean stress upon a variety of materials. From their experimental results for a 0.5% carbon steel it is obvious that on a basis of 5×10^7 reversals, the effect of any mean stress up to 30 Tons/in^2 is comparatively slight. Thus, their results are quite compatible with those of Gould.

Frequency of cyclic stress.

McAdam(21) studied this factor with great thoroughness for several materials in various environments and has expressed his results in a three dimensional form to axes of "stress", "damage" and "frequency".

The relationship is complex, but does show that stress cycles of low frequency are individually more damaging than similar ones of higher frequency. The former obviously allow more time for the conjoint corrosion fatigue action to take place in each cycle. At high frequencies of the order of 10,000 r.p.m. the rate of " damage" is nearly independent of cyclic frequency.

Temperature, salt concentration and oxygen content of corrosive medium.

These three factors are related since oxygen content will vary with the salt concentration, and temperature of the medium. In general, increased damage will tend to result from increased salt concentration, increased oxygen content and increased temperature. Since, however, an increase in either salt concentration or temperature will reduce the concentration of dissolved oxygen, it is not at first apparent which combination of conditions will be most damaging.

Gould(22) studied the influence of temperature on the severity of corrosion fatigue of 0.17% carbon steel in synthetic sea-water. The range of temperature investigated was from 15°C to 45°C and the results show that the endurance limit at any specified number of stress reversals falls with increasing temperature in a manner directly comparable with the increase in weight loss with temperature found in straightforward stressless corrosion tests. This demonstrates the importance of controlling the temperature of the corrosive medium if "scatter" of results is to be minimised.

Gould(23) also investigated the effect of salt concentration by fatiguing mild steel specimens in potassium chloride solutions ranging in concentration from M/100 to 2M. For this range no significant variation in the endurance limit at 10^7 reversals was found. By comparison in high-speed rotor stressless corrosion tests(24) it was noted that more damage was produced in a 0.1 N sodium chloride solution than in a 0.5 N solution, due presumably to the greater solubility of oxygen in the more dilute solution.

Gould suggests that this apparent anomaly can be explained by assuming that since the volume of corrosion product in corrosion fatigue is small, the most concentrated salt solutions will contain more than enough oxygen for the corrosion process.

It seems possible to the author, however, that the explanation lies in the method of testing. Gould's method of wetting the fatigue specimen involves dropping the aqueous medium onto a tape stretched very close to the rotating specimen, so that the meniscus formed between tape and metal is carried round with the rotating specimen. The very thin film of fluid which results must allow diffusion of oxygen from the atmosphere to the metal surface at a rate almost independent of the oxygen content of the fluid. Under conditions of total immersion, however, where the diffusion path is long this independence will not apply and it seems reasonable to postulate corrosion fatigue tests under such conditions would show the influence of salt concentration in a fashion analagous to the stressless corrosion fatigue tests discussed above.

CHAPTER IV.

THEORIES OF CORROSION FATIGUE.

In the present state of knowledge, no quantitative theory of corrosion fatigue is available such as would allow the endurance of a specimen at a given stress range to be estimated by reference to fundamental properties of the metal and its environment. Numerous workers in this field, however, have endeavoured to explain their results qualtiatively in terms of the mechanism of the process.

Thus, Gough(11), in considering the mechanism of corrosion fatigue, accounts for the vastly increased rate of corrosion under these conditions as being, "largely due to the effect of the cyclic strains on the porosity and rupture of the wholly or weakly protective films that tend to form under corrosion conditions". On this he bases his conception of a two-stage phenomenon.

In the first stage, the differences in potential existing between different areas on the metal surface lead to corrosion currents with consequent loss of metal at the anodic areas. The tendency of the corrosion product, more particularly the thin primary film rather than the secondary products of corrosion, to shield these areas from further action is overcome by the cyclic strain which promotes further loss of metal at these points. In this way, the attack is concentrated on localised areas, so producing pitting. The development of these pits into deeper, sharper forms may be accelerated by the "oxygen differential" existing between the bottoms of the pits and the main metallic surfaces. Thus, the pits will assume a form which causes stress concentration at their bases, such that a crack is initiated.

This represents the second stage of Gough's mechanism of failure. Subsequently, this crack will spread as in normal fatigue until the remaining cross-sectional area of the specimen fails under the principal stress.

McAdam(25) has developed a concept which differs from that of Gough. Although he recognises the two stages of the process, firstly pitting and then stress concentration at the bottom of the pits, he considers the pitting to result because, "the effective solution pressure is higher in a specimen under cyclic stress than in a specimen not under stress." By this he implies that stressed metal is inherently more anodic than unstressed material. While this is true, it is difficult to see how this could cause localised pitting in a specimen whose surface was uniformly stressed. McAdam does agree, however, that "this increase in effective solution pressure may be due in part to the continued removal of a protective film."

Gough and Sopwith(26) considering the corrosion fatigue of single and bi-crystal specimens of aluminium in tap-water, showed that the failure of the specimens "took place primarily by the formation of cracks in areas undergoing heavy plastic deformation." These cracks were shown generally to lie parallel to the traces of operative slip planes. In several cases, they originated at holes situated at the most highly stressed region, but no evidence was available of the origin of these holes. The experiments did show, however, that the intercrystalline boundary was not attacked by the corrosive medium, nor did it influence in any visible manner the method of failure of the specimen.

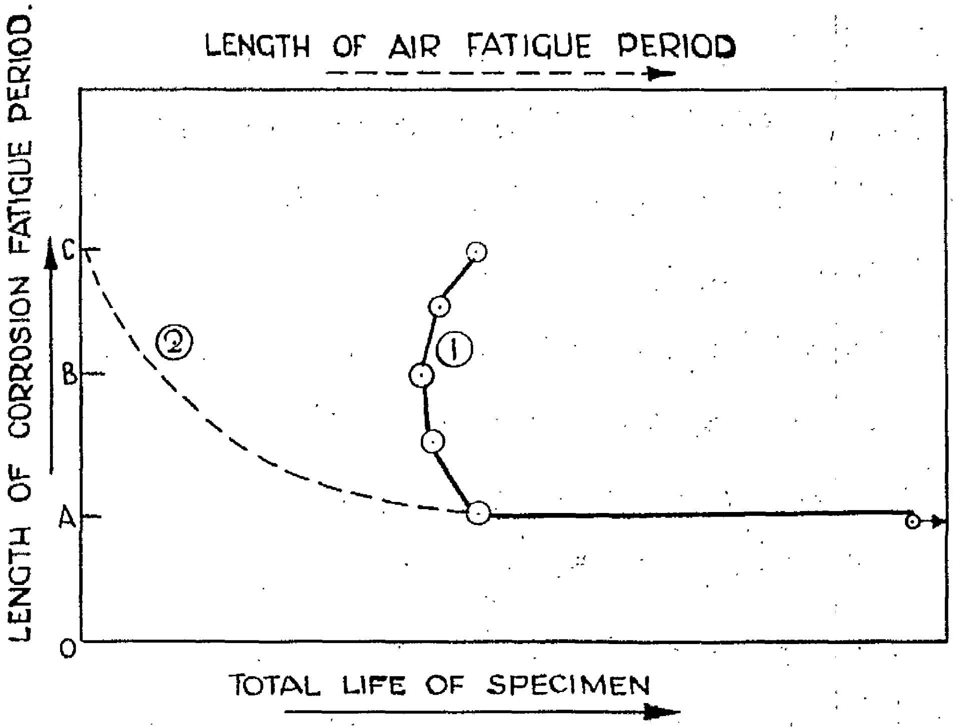


FIG. 1. RESULTS OF TWO-STAGE CORROSION FATIGUE EXPERIMENTS ON MILD STEEL (AFTER EVANS & SIMNAD).

Evans and Simnad(27), working on the corrosion fatigue of 0.19% carbon-steel wire specimens wetted with N/10 potassium chloride solution, produced some interesting results. By using a two-stage procedure, a period of corrosion fatigue followed by a period of fatigue in air only, at the same stress, until fracture occurred, they were able to show the effect of the length of the corrosion fatigue period on the total life of the specimen. The type of relationship obtained is illustrated in Curve(1), Fig.I. It can be seen that for periods of corrosion fatigue less than OA the total life is infinite. For periods between OA and OB, the total life decreases, but for periods between OB and OC it increases again.

Evan and Simnad suggest that during the period up to B, one "pioneer" crack is developing to the exclusion of others and it continues to deepen and sharpen until the increase in electrical resistance between top and bottom of the pit outweighs the increase in potential with depth. At this stage further cracks start to develop and these relieve some of the stress concentration at the base of the pioneer pit, so that the specimen is less liable to fail under the fatigue action. Theyidentify the period OB as that in which the pioneer crack develops and the period BC as that in which secondary cracks develop.

While the theory is plausible, it must be pointed out that Curve (1) is misleading. The total life is the sum of the first and second stages of the test and if the length of the first stage is subtracted from the total life, Curve (2) is obtained. This shows the relation between the corrosion fatigue period and the subsequent fatigue life in air at the same stress, and at no value of first period length is there an increase in the <u>subsequent</u> life of the specimen, as might be expected if the "pioneer" crack postulate were valid. The turning value in Curve (1), corresponding to the ordinate OB, results from the slope of Curve (2) exceeding 45°, i.e., after a first stage period greater than OB, the shortening of the second stage takes place less rapidly than the increase of the first stage.

The other conclusions of Evans and Simnad are of interest. They consider that their results show that at least three different factors operate in causing alternating stress to enhance the rate of corrosion and the rate of mechanical damage.

These are:-

(1) Diminution of cathodic polarisation (by improvement in supply of oxygen to cathode).

(2) Diminution in anodic polarisation (by rupture of protective films).

(3) Diminution of the resistance of the path joining anodes and cathodes (by removal of corrosion products, and possibly by film rupture).

Evans suggests that there may be yet a further factor in operation, namely:-

(4) A bodily shift of the anodic polarisation curve in the direction of the baser metal (due to the distortion or obliteration

of the crystalline structure of the metal which thus becomes less stable and more reactive).

Whitwham and Evans(28) carried out a series of tests with the object of deciding whether or not a period of fatigue in air produced an increased susceptibility to failure by corrosion fatigue, e.g., by the production of disarrayed material along slip bands which would be especially liable to subsequent corrosive attack. They found no shortening of corrosion fatigue life due to a preliminary period of air fatigue and, indeed, a slight improvement in corrosion fatigue life where the stresses used in the air fatigue period were less than the fatigue limit. They concluded that the special susceptibility of the disarrayed material produced locally along small slip bands may account, at least partly, for the phenomenon of corrosion fatigue, but this material is susceptible to attack "only if the corrosive liquid acts upon it while the atoms are on the move and while the liquid at the top of the advancing crack is very hot".

Simnad and Evans(29) investigated the corrosion fatigue life of mild steel wires wetted by N/10 hydrochloric acid. They studied the results of two-stage tests, measuring electrode potentials and corrosion rates. In acid solution, the factors associated with film formation and destruction do not apply, any oxide layer being dissolved. In this way they isolated the influence of "disarrayed" material on the corrosion fatigue characteristics and found that after a lengthy incubation period, relatively greater at high than at low stresses; "cracks develop, the fatigue strength drops catastrophically, the rate of chemical corrosion, hitherto constant, greatly increases, whilst the potential is shifted in the base-metal direction". That work supports their view that "although elastic deformation does not affect the chemical or electrochemical properties of the iron, deformation beyond the ekastic limit, which may occur if pits produce stress intensification, alters these properties, making the iron behave like a more reactive metal".

The views of Evans and his associates could be summarised to give the following picture of the corrosion fatigue process.

Initially, on exposing a metal to corrosion fatigue conditions, the surface oxide film is broken down by the action of cyclic strain so that certain areas of the metal surface are exposed to the action of the corrosive medium. The cyclic strain prevents the repair of the oxide film in these areas and dislodges corrosion products from them so that hemispherical pits rapidly develop.

Although the stress concentration in this form of pit is small, there will be a tendency for the material at the base of the pit to become increasingly anodic to the remainder of the metal surface. This tendency will be supplemented by the potential supplied by the differential aeration cell caused by the lack of oxygen at the bottom of the pit and the plentiful supply of oxygen at the main actively cathodic surface. Thus, the rounded pits will deepend and sharpen and assume the crevice form associated with corrosion fatigue.

The stress concentration at the bottom of such crevices will be high and eventually regions of slip will develop there. This will offer disarrayed, energy-rich, strongly anodic material to the corrosive medium, and rapid destruction of the metal in a direction parallel to the operative slip planes in the particular crystal concerned will follow. The fissure thus formed will spread with increasing velocity as the stress concentration increases and yet more strongly anodic material is subjected to the corrosive attack. Eventually, when the stress concentration reaches a high enough value, the fatigue action may develop so quickly that it runs ahead of the accelerated corrosion until failure occurs.

A series of experiments by Karpenko(30,31,32) has yielded striking results and these deserve careful consideration. Stress-endurance curves were obtained for steel in air, in distilled water, in distilled water plus 1.0 per cent saponin, and in these last two media with the specimens cathodically protected by zinc strips. Examination of these curves suggests that two distinct phenomena are involved. Karpenko terms these adsorption fatigue and corrosion fatigue.

Adsorption fatigue is produced when the fluid medium is sufficiently surface-active to enter the ultra-microscopic cracks which ocpn up on the specimen surface during the tensional half-cycle of the applied stress. During the compressional half-cycle, this adsorbed fluid is expelled from the cracks but resists expulsion and so weakens the cohesive forces among the surface elements of the metal, thus assisting the development of the initial defects into fatigue cracks proper. Karpenko has found this process to be frequency dependent, and to produce a stress-endurance curve with a horizontal asymptote of stress analagous to but considerably lower than the fatigue limit in air. He obtained such curves for the zinc-protected specimens tested in water and in water plus 1 percent saponin. These gave true fatigue limits 22 percent and 30 percent lower, respectively, than the fatigue limit in air. The marked influence of saponin is attributed to its surface-active properties.

The stress-endurance curves produced by Koupenko for unprotected steel in distilled water and in water plus 1 percent saponin are of the form normally associated with corrosion fatigue. They show no evidence of approaching an asymptote of stress, and endurance limits at 20 x 10^6 reversals are respectively 34 percent and 43 percent lower than the fatigue limit in air. Since it is held that the saponin cannot increase the rate of corrosion, the lowering of the endurance limit in its presence can be attributed solely to its surface active properties.

To summarise Karpenko's views then, he considers that the corrosion fatigue stress-endurance curve as normally determined for aqueous media is a summation of the adsorption fatigue characteristic for water and the true corrosion fatigue characteristic for the metal and the medium concerned. The first effect is purely a physical one while the second is electrochemical.

CHAPTER V.

THE INHIBITION OF CORROSION FATIGUE.

The possibility of reducing corrosive attack by the addition of chemicals to the corrosive medium has long been recognised. An early demonstration of this by Friend and Brown(33) showed that the addition of potassium chromate to sodium chloride solutions substantially reduced the corrosion of pure iron. Such additions are termed corrosion inhibitors and the subject of inhibition by chemical means has since been extensively studied. In particular, the electrochemistry of the process has been examined by Evans(34,35), Mears(36), Hoar(37), and others.

Classification of Inhibitors.

Several methods of classifying inhibitors have been suggested but in the present state of knowledge of the subject it is difficult to justify one rigid system. It should be possible, when further knowledge is acquired, to classify these substances according to the particular mechanism involved in their inhibiting action. This has already been proposed by Pourbaix and Rysselberghe(38) who favour the following division of inhibitor types.

1. Surface conversion inhibitors, e.g., antimony and arsenic salts, chromates, nitrites, phosphates.
2. Adsorption inhibitors, e.g., thiourea and certain amines, soluble oils.
3. Diffusion inhibitors, e.g., gelatin, casein and certain colloids.

Evans(35) classification into anodic and cathodic inhibitors according to whether they affect the degree of polarisation at anode or cathode can be used as a further subdivision within the above system.

Hackerman(39) classifies inhibitors according to their chemical constitution, e.g., "Inorganic Chemicals" and "Organic Chemicals" with further subdivision on the basis of whether they are "oxygen containing", "nitrogen containing", "sulphur containing", etc.

Uhlig(40) draws a distinction between inhibitors and passivators according to the strength of the adsorption bond between metal and inhibiting agent, but broadly speaking this distinction is made between types (1) and (2) in the system advocated by Pourbaix and Rysselberghe.

Theories of Inhibition.

The most widely accepted postulate involves the formation of surface layers or films on the metal which increase the degree of polarisation at anode or cathode, such that the electrochemical corrosion reaction is stifled. The nature of this layer or film, however, for any particular inhibitor is still a matter of controversy in many cases.

Uhlig(40) in discussing the value of chromate in inhibiting the corrosion of steel in water has recently suggested that a bonded layer of chromate ions, only one molecule thick, forms on the iron surface. The valency bond forms between the surface iron atoms and two of the oxygen atoms in each chromate ion, but the metal surface remains intact so that no stoichiometric compound is formed. While this postulate is of considerable interest, it has been more usual to regard the surface layer as being formed of a mixed iron-chromium oxide, which adheres strongly to the iron surface forming a thin but not necessarily monomolecular protective layer.

Mayne, Menter and Pryor(41) investigated the inhibition mechanism when iron was exposed to the action of sodium hydroxide solution. Using the electron microscope to produce electron diffraction patterns, they studied the composition of the films that formed when specimens, entirely freed from their original air-formed oxide film, were immersed in 0.1 N sodium hydroxide solution containing dissolved oxygen. They found that a thin film of γ Fe_2O_3 (containing some γ $Fe_2O_3.H_2O$) was formed under these conditions, and suggest that the inhibition of corrosion as measured by specimen potential was accounted for by this film. They further suggest that this film formed as the result of a heterogeneous reaction between dissolved oxygen and the iron specimen.

Mayne and Pryor(42) have also investigated the film formed on initially film-free iron by solutions of chromic acid and potassium chromate containing dissolved oxygen, and found it to consist mainly of γ Fe_2O_3. This experimental work tends to negative Uhlig's suggestion of a valency-bonded monomolecular layer, mentioned earlier.

Cohen(43) studied the effect of sodium nitrite additions on the corrosion of steel in tap-water and concluded that "The mechanism of inhibition is probably the formation of a tight oxide layer which is formed by the combined action of nitrite and oxygen and is repaired by the nitrite".

Palmer(44) in an interesting study of the inhibitive properties of chromate-phosphate mixtures, attributed their action to the precipitation of a crystalline ferric phosphate deposit on the weak spots in the original film on the steel specimens used. This implies that the oxide layer covering the specimen surface is of some considerable thickness (referred to a molecular scale) and the protective action is due to a physical barrier built up between the metal and the corrosive medium.

Adsorption is frequently suggested as the mechanism involved where organic polar compounds are used as inhibitors. Some difference of opinion exists, however, regarding which areas of the metal are concerned in the adsorption phenomenon. While some investigators consider adsorption to occur mainly at anodic points, others suggest that an all-over monomolecular film is formed protecting anodic and cathodic areas alike. Hamer, Powell and Colbeck(45) try to reconcile these views in a combined film-precipitation theory suggested by their work on the use of oil emulsions as corrosion inhibitors.

The dangers of "pitting" attack which may arise from the use of insufficient anodic inhibitor have been clearly stated by Evans (34,35), on several occasions. The danger is inherent in any efficient inhibitor where its concentration falls below that required to give complete protection. Under these conditions a small anode is exposed to a large cathode and although the total corrosion rate may be very low, the concentration of the attack on small areas causes "pitting". In the presence of cyclic stress this would be expected to lead to early failure.

While cathodic inhibitors are, in this respect, much safer, they are inherently less efficient in their inhibiting action, due to the indirectness of their control on the corrosive reaction and to the vastly greater surface area they are required to inhibit.

Inhibitors in Use.

Very little experimental data is available on the effect of corrosion inhibitors on the corrosion fatigue properties of steels in aqueous media. In consequence, a student of this subject must, of necessity, depend for guidance upon the more extensive work which has been carried out on the inhibition of corrosion in the absence of stress. Great caution must, however, be exercised in assessing the possible efficacy of an inhibitor under corrosion fatigue conditions, from data obtained under stressless corrosion conditions. The notes on individual inhibitors which follow are concerned mainly with stressless conditions, and where corrosion fatigue tests have been carried out this is specifically mentioned.

Chromates.

The use of chromates and dichromates as industrial corrosion inhibitors is widespread and Speller, McCorkle and Mumma(46) have investigated their usefulness under corrosion fatigue conditions in the presence of chloride. They showed that even in 3% sodium chloride, roughly corresponding to natural sea-water, considerable extension of specimen life was produced by 0.5% chromate addition. A comparison between chromate and dichromate additions showed the former to be the more efficient.

Gould and Evans(47) also investigated the inhibiting influence of chromate in the presence of chloride, and showed clearly that the amount of chromate required increased greatly as the chloride content rose. In concentrations equivalent to sea-water, however, the extension of specimen life was not sufficient to class this inhibition as entirely satisfactory for practical purposes.

Roetheli and Cox(48) established that, in general, increase of salt concentration or temperature increased the minimum concentration of chromate required to give overall protection.

Phosphates.

Hatch and Rice(49) discuss the use of glassy phosphates of the "Calgon" type (sodium hexametaphosphate) as corrosion inhibitors. They found these to give considerable protection against stressless corrosion if a sufficient rate of supply of phosphate to the metal surface was maintained. No work under corrosion fatigue conditions is recorded.

Chromate-Phosphate Mixtures.

Chromate-Phosphate Mixtures.

Palmer(44) has shown that a mixture of phosphate and dichromate is more effective in preventing corrosion than either inhibitor alone. Similar results, later published by Kahler and George(50), confirm that this "di-anodic" treatment, as they term it, actively prevents the "pitting" which so often accompanies the use of anodic inhibitors. The results indicate that the treatment should be used within the pH range 5.5 to 7.3. No test of this inhibitive mixture has been made under corrosion fatigue conditions.

Silicates.

Stericker(51) has studied the use of silicates as inhibitors in domestic water systems and in brine pipe-lines. Economically, this inhibitor is applicable to "once through" water systems, since small dosages substantially curtail corrosion losses. In circulating systems, however, silicate does not inhibit so efficiently as, say, chromate and it would presumably be even less efficient under corrosion fatigue conditions.

Nitrites.

Wachter(52) presents experimental data on the inhibiting powers of sodium nitrite on the corrosion of steel in chloride solutions. He found that for complete protection, a ratio of nitrite to chloride by weight of at least unity had to be maintained.

Cohen(43) made a thorough investigation of the use of nitrite and concluded that the concentration required for inhibition increased with temperature but decreased with increasing rates of flow. He noted, too, that in common with other anodic inhibitors too low a concentration could lead to "pitting".

Wyllie and Cheesman(53) also investigated the use of sodium nitrite as an inhibitor in sea-water and found it effective at concentrations around 1%. Even, more effective, however, was a phosphate-nitrite mixture which protected completely steel specimens immersed in 50% artificial sea-water at a pH of 7.0 to 8.0.

Cathodic Inhibition.

Thornhill(54) in an investigation into the efficiencies of various metallic salts as cathodic inhibitors, studied the cations, Fe", Mg", Ca", Co", Sn", Ba", Zn", Mn" and Cr". Only the last three showed any inhibiting capacity, and of these none reduced the corrosion by more than 30%. These tests were carried out under stressless conditions and in view of the poor results obtained, it seems unlikely that they could be used successfully to inhibit corrosion fatigue. Fink, Turner and Paul(55), showed "Zinc Yellow" to be beneficial at very low salt concentrations in the inhibition of corrosion fatigue, but at higher salt concentrations, no success was achieved with this inhibitor.

Soluble Oils.

Hamer, Powell and Colbeck(45) found that 0.5% of oil added as emulsion to a corrosive water gave considerable protection from normal stressless corrosion. The action would seem to be more anodic than cathodic and the attendant danger of "pitting" at lower concentrations has been demonstrated. The effect of high chloride contents would not appear to have been investigated, but it is likely that chloride ion would decrease the stability of the oil emulsion.

PART II.

EXPERIMENTAL ASPECTS.

CHAPTER VI.

THE DESIGN AND CONSTRUCTION OF APPARATUS.

KEY.

Ⓐ	$\frac{1}{8}$ H.P., 230V. A.C. MOTOR
Ⓑ	PULLEY BELT.
Ⓒ	PLASTIC CENTRIFUGAL PUMP.
Ⓓ	SILICA TUBE.
Ⓔ	RESISTANCE HEATER WINDING.
Ⓕ	THERMOSTAT VESSEL.
Ⓖ	THERMOMETER
Ⓗ	PYREX TANK.
Ⓙ	THERMOSTAT.
Ⓚ	MILD STEEL SPECIMEN.
Ⓛ	SPECIMEN CLAMP.
Ⓜ	PYREX RESERVOIR TANK.
Ⓝ	CORROSIVE MEDIUM.

NOTE :- ALL CONNECTIONS MADE WITH $\frac{1}{2}''$ i.d. P.V.C. TUBING.

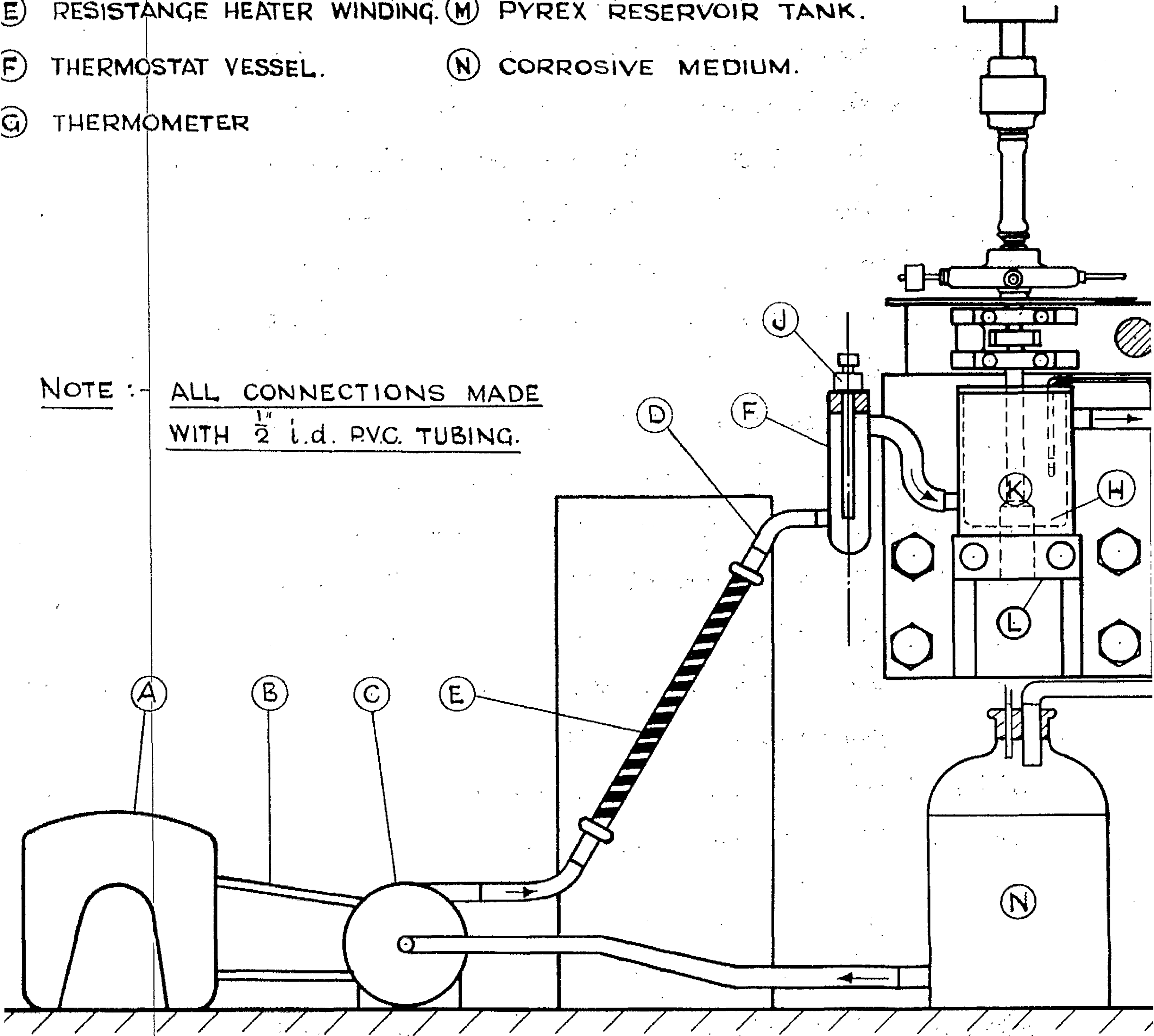


FIG. 2. GENERAL ARRANGEMENT OF CORROSION FATIGUE APPAPATUS.

Considerations Influencing Design.

The experimental programme described in this thesis was inspired by the occurrence of corrosion fatigue failures in water cooled marine Diesel engine piston rods. In order to relate experimental results to service conditions it was decided that material, temperature and flow conditions should be reproduced so far as possible. This required that the specimens be manufactured from a low-carbon steel with an ultimate Tensile Stress value of 28.0 to 32.0 tons per square inch, and that the fully aerated aqueous medium should flow continuously over the specimen surface at a temperature of 88°C.

Since many practical failures had occurred after considerable periods of service it was considered that conditions influencing corrosion fatigue life up to 50×10^6 stress reversals should be investigated. It was not possible, however, to reproduce practical frequencies of stress reversal of the order of 110 r.p.m. as this would have involved inordinately long test runs, and accordingly a test frequency of 3000 r.p.m. was adopted.

A consideration of prime importance was that no other metals be introduced into the corrosion circuit since these could influence the rate of corrosion of the specimen.

General Description of Apparatus.

General Description of Apparatus.

Figure 2 illustrates the general arrangement of the experimental equipment. This comprises a rotating load fatigue machine fitted with a glass tank sealed around the specimen such that a corrosive

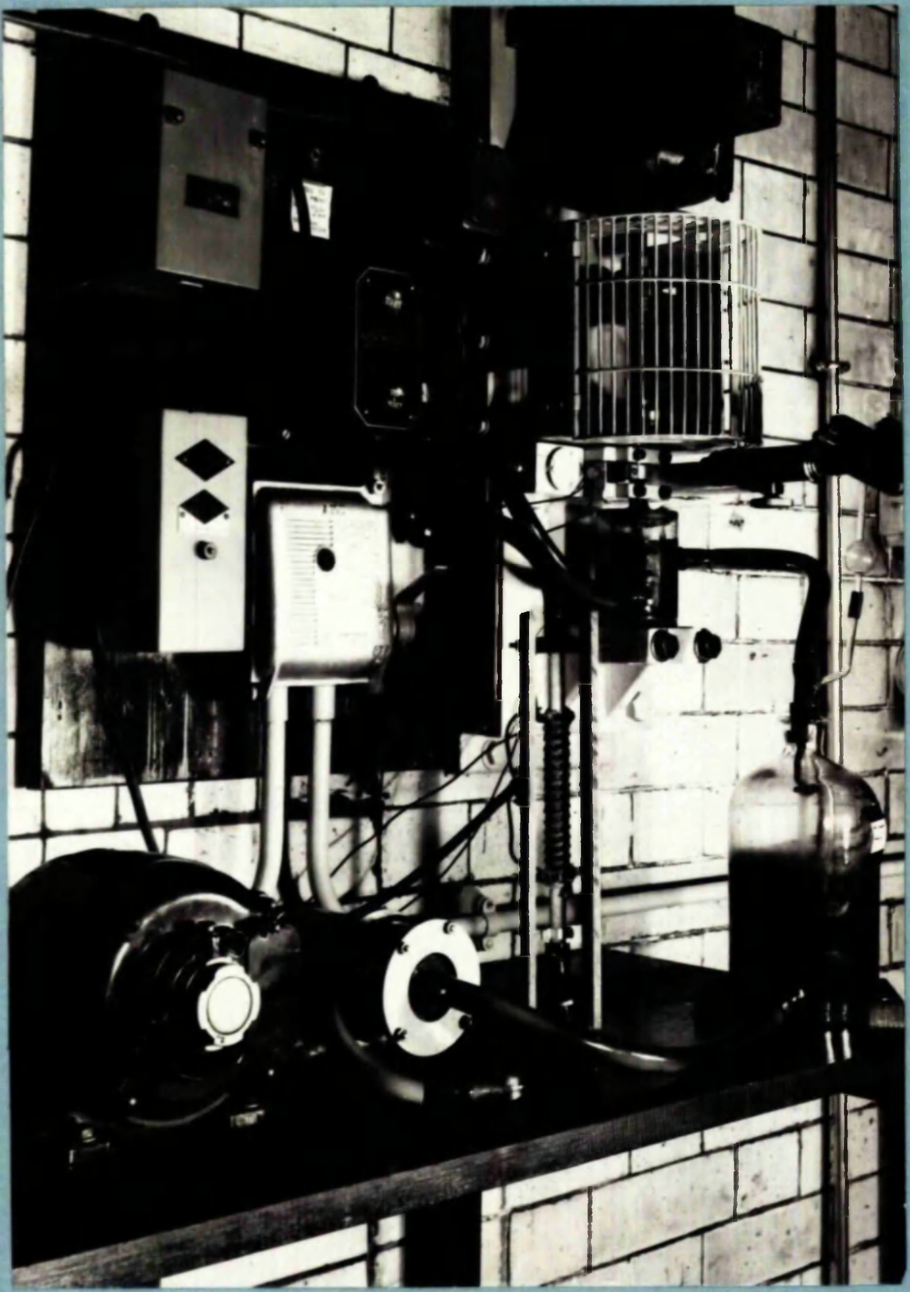


PLATE 2. CORROSION FATIGUE APPARATUS.

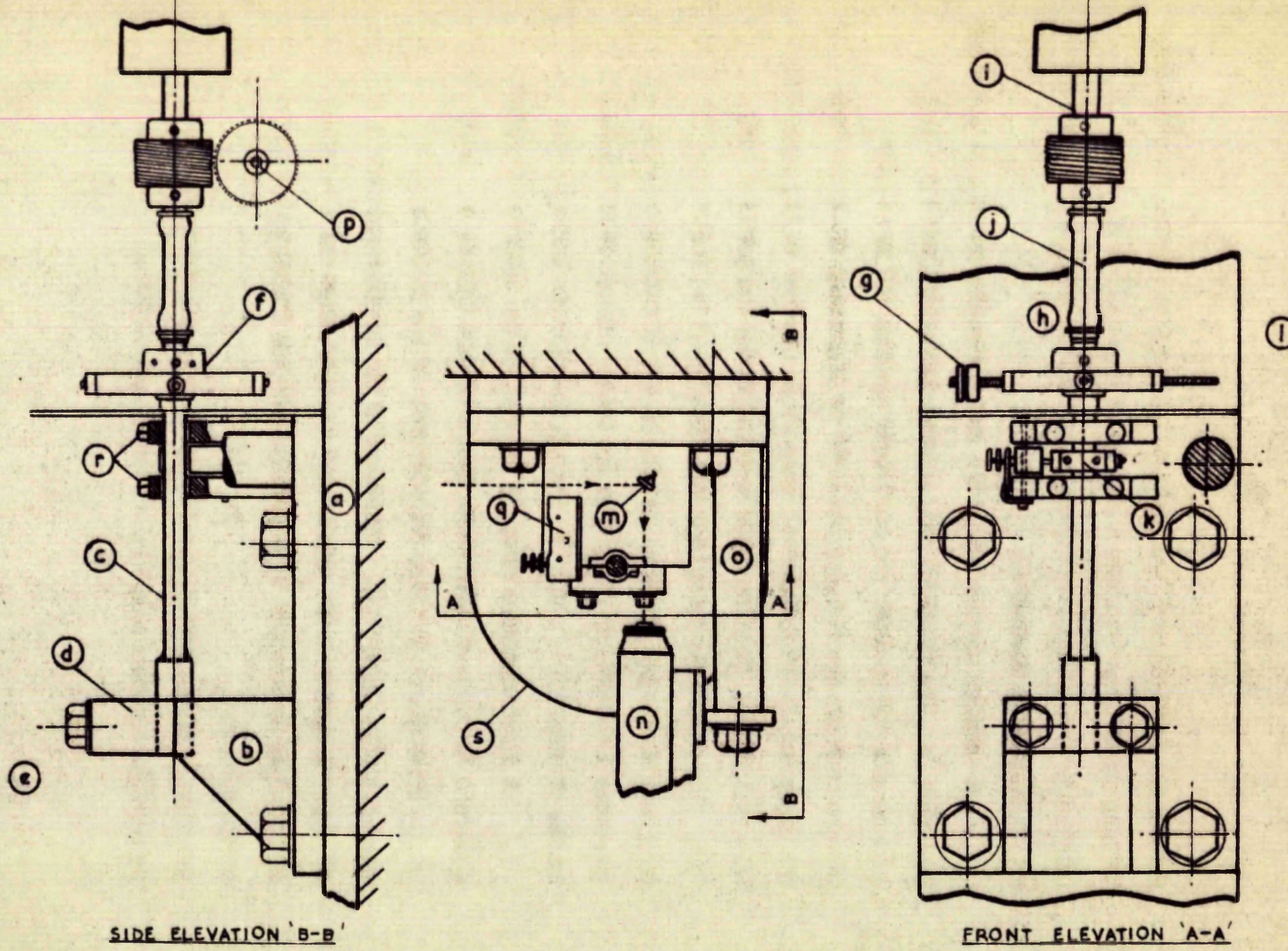
solution may be circulated over the specimen surface. The solution, drawn from a two-litre asperator bottle by a non-metallic centrifugal pump is passed through a tubular heater and over a thermostat element into the specimen tank from which it overflows back to the reservoir. The connecting tubes used in the fluid circuit are of Polyvinylchloride which is satisfactorily resistant to heat and chemical reaction with sea-water and oxidising inhibitors.

The use of a reservoir was necessitated by the need to maintain an adequate relation between solution volume and specimen surface area, such that concentration or depletion of the solutes during test was minimised.

Testing specimens to a limit of 50 million stress reversals at 3000 cycles per minute involved almost twelve days continuous running of the equipment. Since this length of test offered a serious limitation to the experimental programme, a further five sets of equipment were constructed during the course of the investigation, the original prototype having been first fully tested for long term reliability. Plate 2 shows this first equipment and the following sections present details of the construction of its component parts.

Fatigue-Testing Machine.

The rotating-load fatigue-testing machine designed by the British Non-ferrous Metals Research Association was adopted as being most suited to the proposed investigation. The use of this machine for elevated temperature fatigue testing has been described by



SIDE ELEVATION 'B-B'

FRONT ELEVATION 'A-A'

FIG. 3. THE B.N.F.M.R.A. ROTATING LOAD FATIGUE-TESTING MACHINE

McKeown and Back(56) who suggested that it could be adapted for corrosion fatigue conditions. A major advantage of this machine was the simplicity of fluid sealing arrangements which it permitted by virtue of its stationary specimen.

A detailed arrangement of the fatigue-testing machine is presented in Figure 3. The baseplate "a", mounted vertically, carries a cast iron bracket "b" to which the cantilever specimen "c" is rigidly attached through the clamping piece "d" by tightening the bolts "e". The upper end of the cylindrical specimen is attached to the inner race of a ball bearing on whose outer race is carried the rotating head "f". The adjustable weights "g" are threaded on the radial arm "h" of the rotating head and these provide an out-of-balance mass which generates a centrifugal force when the head is driven at 3000 r.p.m. by the electric motor shaft "i" through the flexible coupling "j".

A light aluminium clamp "k" carried on the specimen contains a pinhole "l" through which light from a 12 volt bulb is reflected by the steel mirror "m" into the objective of the microscope "n" carried on the pillar "o". Vibration of the specimen causes a band of light to appear in the eyepiece of the microscope and the length of this band as measured by adjustable shutters fitted to the microscope head may be related to the amplitude of vibration. In practice, a direct calibration between band length and applied load is possible and this will be discussed in detail later.

FULL SCALE.

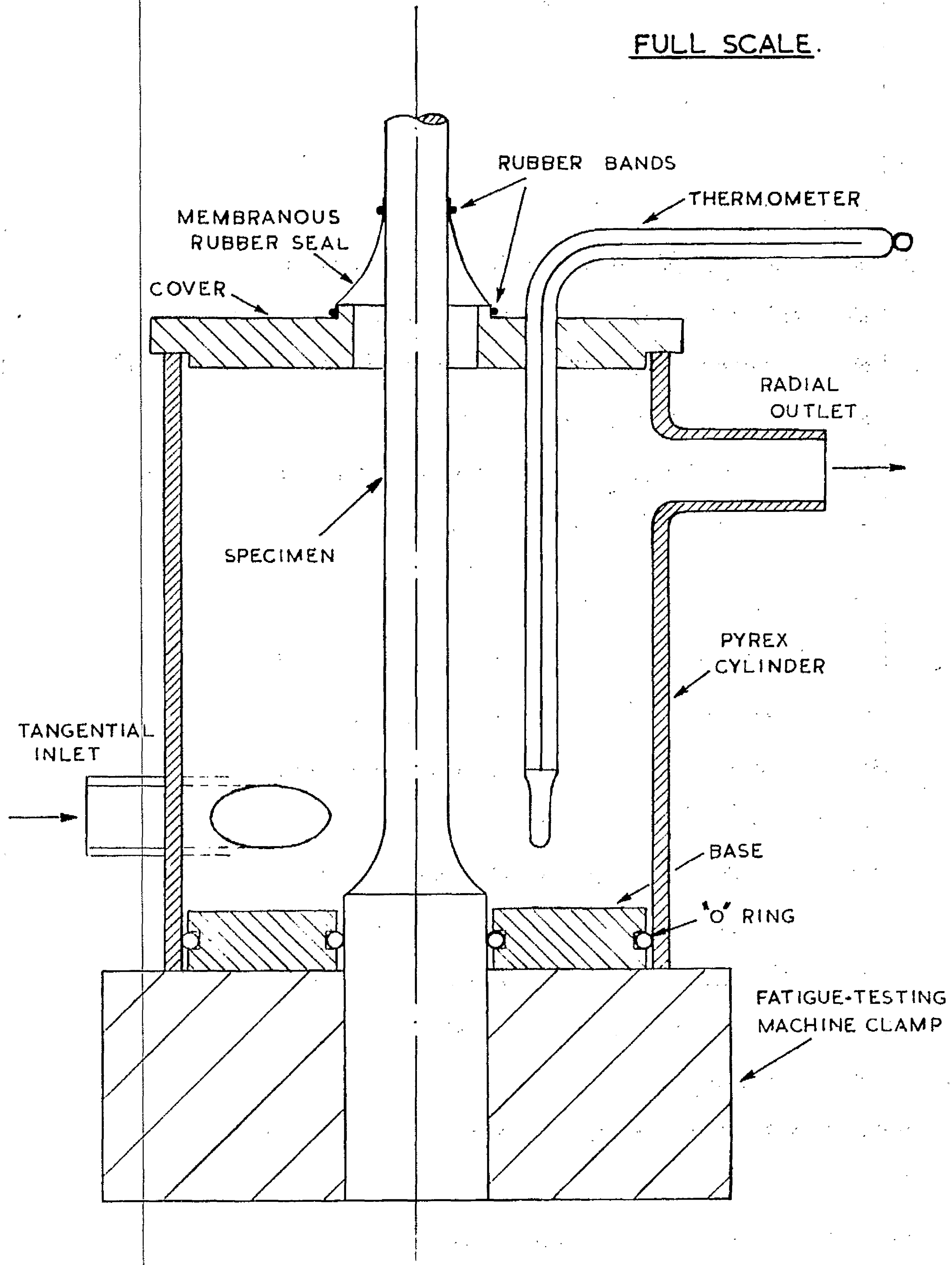


FIG. 4. SPECIMEN TANK.

The number of revolutions to fracture is recorded on a six-digit counter driven through the 100:1 reduction worm and wheel gear "p". The increase in vibration amplitude which is characteristic of the onset of fatigue failure in a constant-load machine is used to trip the micro-switch "q" which cuts off the current to the driving motor through a relay system. The guards "r" bolted to the bracket "b" serve as an added precaution should the specimen fracture completely before the motor comes to rest. A further safeguard on this equipment is the perspex cage "s" which enclose all the rotating parts.

Specimen Tank.

The method used to enclose the fatigue specimen in an aqueous medium is illustrated in Figure 4. A specially moulded pyrex cylinder, three inches in diameter, surrounds the specimen clamped in the fatigue machine. A cylindrical base, machined from polyester resin, is sealed around the specimen shank, which passes through it, and into the pyrex tank by synthetic rubber "O" rings. The elasticity of these rings compensates for the differential thermal expansions of glass, metal and resin which operate during the heating up and cooling down of the corrosive medium.

The medium is pumped into the tank through the tangential inlet and overflows through the radial outlet. A cover of the same material as the base fits loosely into the top of the tank and where the specimen passes through this, a fine membranous rubber seal prevents the loss of fluid by evaporation without sensibly restricting the movement of

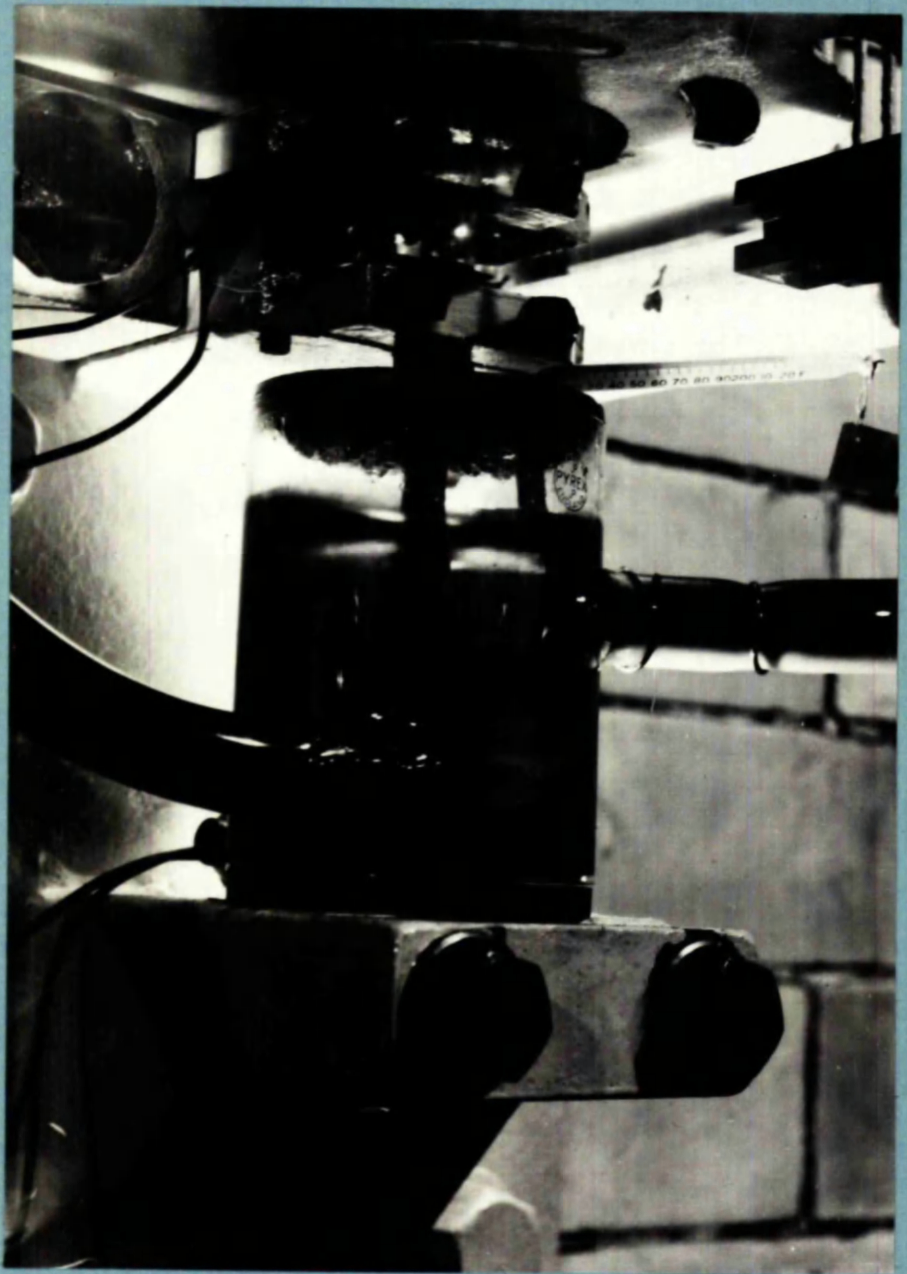


PLATE 3. SPECIMEN TANK.

the specimen. The cover also carries a thermometer on which the temperature of the fluid is registered. Plate 3 shows a close-up view of the tank in operation.

Fluid Circulating Pump.

Since it was considered necessary to prevent contact between the corrosive medium and any metallic surface other than the specimen, a circulating pump of non-metallic construction was required. Of the pumps available commercially none were of suitable capacity and, accordingly, a specially designed pump was constructed.

Early attempts to coat the brass components of a small centrifugal pump with impervious lacquers proved unsuccessful. Brittle coatings were found to crack from the sharp corners of the impeller blades, while softer materials did not withstand the erosive action of the circulating fluid.

A small centrifugal pump was subsequently constructed by machining the components from ebonite. Although short term soak tests had suggested that ebonite was dimensionally stable in water at 90°C. this pump was unsatisfactory in practice. On prolonged exposure to water at this temperature, swelling of the ebonite reduced the clearance between impeller and casing until seizure resulted. Re-machining of the components produced only a temporary improvement, seizure again resulting after several days continuous running.

A polyester resin, supplied by Messrs. Bakelite Ltd., was later found to possess suitable properties and pump components were manufactured from this. The resin was supplied in liquid form which

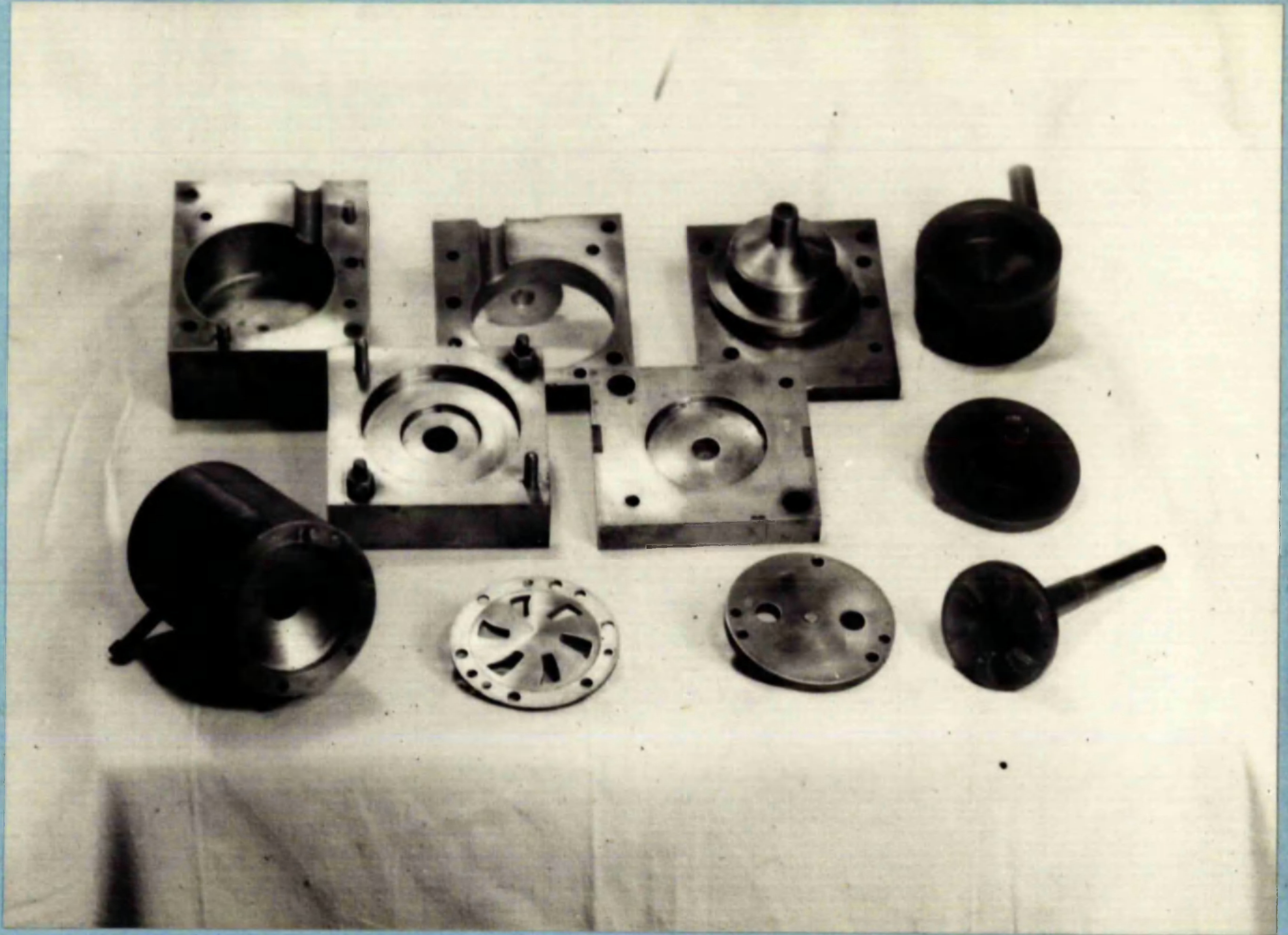


PLATE 4. STEEL DIE-MOULDS AND POLYESTER RESIN PUMP COMPONENTS.

polymerised upon the addition of a catalyst, the process being aided by a chemical accelerator and the application of heat. China clay in finely divided form was added as a "filler" giving improved machinability and resistance to shock.

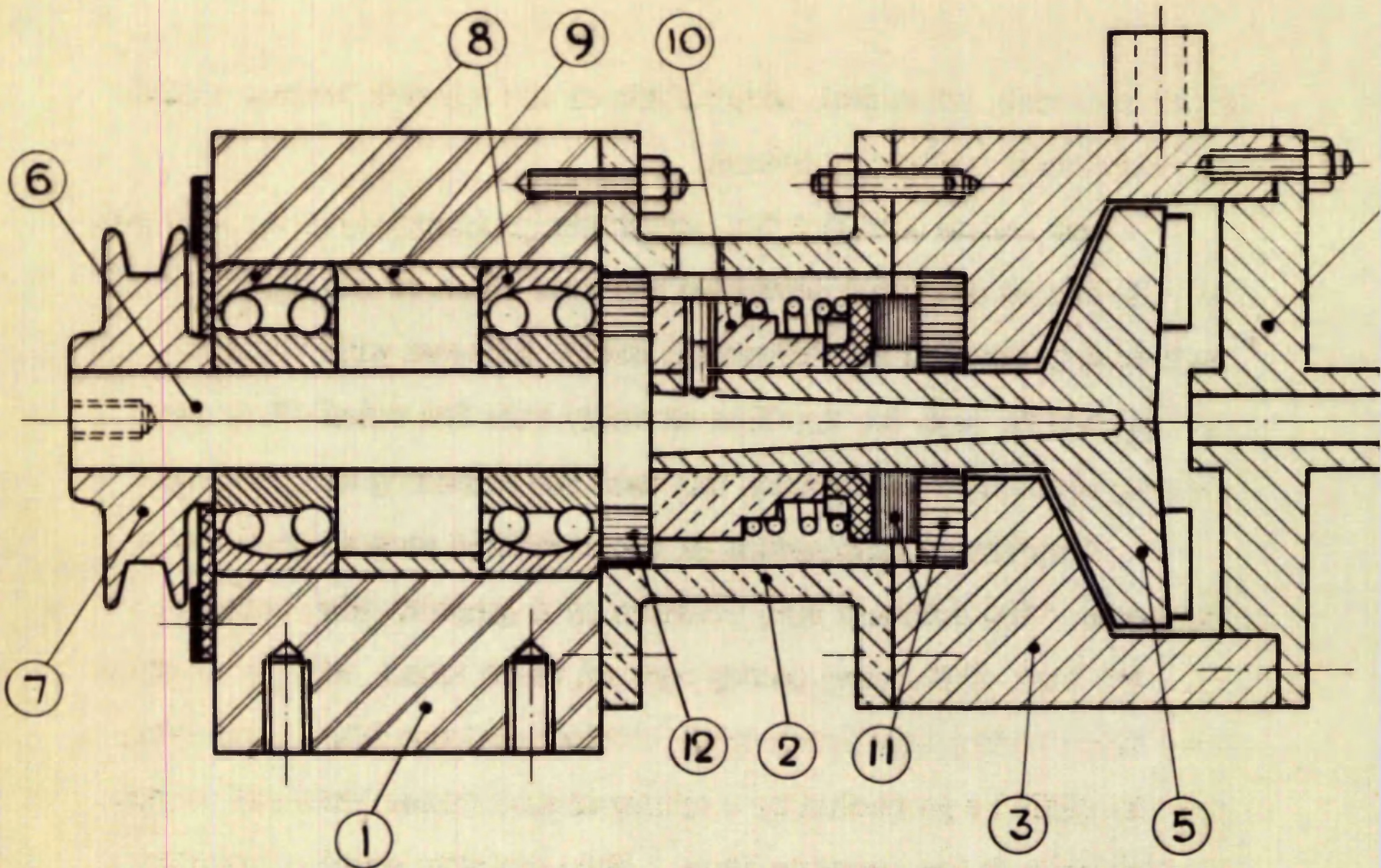
The successful casting of the components was made difficult by the two percent contraction involved in the polymerisation reaction. After repeated attempts, the following mixture and method were found to prevent cracking.

Casting Mixture.

Bakelite Polyester Resin	SR 17449	100 gm.
Bakelite Accelerator	SR 17448	2.5 gm.
Bakelite Catalyst	SR 17447	1.0 gm.
Powdered China Clay		40.0 gm.

This mixture was poured into specially constructed steel die-moulds which were then placed in an air-oven held thermostatically at a temperature of 40°C. After eight hours, the temperature was raised to 100°C for a further two hours before the moulds were stripped. The pump casing mould required to be stripped hot since the thermal contraction on cooling was sufficient to crack the hollow component if the steel core were left in position.

The tendency of the resin to adhere to the steel surfaces was overcome by the use of silicone grease as a separating agent. The problem of applying this agent uniformly to the mould walls was solved by brushing a solution of the grease in carbon tetrachloride over the



① M.S. BEARING HOUSING.
② BRASS GLAND HOUSING.
③ PLASTIC PUMP CASING.
④ PLASTIC PUMP COVER.
⑤ PLASTIC PUMP IMPELLER.
⑥ M.S. DRIVING SHAFT.

⑦ ALUMINIUM DRIVING PULLEY
⑧ DRIVING SHAFT BEARINGS.
⑨ DISTANCE PIECE
⑩ "MORGAN-STUART" GLAND.
⑪ GRAPHITE BEARING RINGS
⑫ BEARING SEAL.

FIG. 5. NON-METALLIC CIRCULATING PUMP

steel surfaces, subsequent evaporation of the solvent leaving a thin but continuous coating of grease.

The moulds used and the components produced are shown in Plate 4. It may be seen that advantage has been taken of the casting technique to produce the tangential outlet integral with the pump casing, and to cast the impeller directly onto the reinforcing steel driving shaft thus eliminating the need for machining and fitting.

A sectioned arrangement of the assembled pump is given in Figure 5. The rotating seal consists of a graphite ring cemented into the back of the pump casing against which bears another graphite ring keyed to the impeller shaft. Leakage between this latter ring and the shaft is prevented by a spring-loaded rubber "trumpet" washer bearing against the graphite ring. This assembly rotates with the impeller shaft which is driven by belt and pulley from a one-eighth horsepower electric motor. At a speed of 2000 r.p.m. the pump delivers six litres per minute through the experimental circuit.

Heater and Thermostat.

Since the need to avoid the presence of metal in the fluid system precluded the use of immersion heating elements, a fluid heater was constructed by winding a 750 watt electric resistance element around a twelve inch length of half-inch bore fused silica tube. Asbestos string wound parallel with the element served to prevent contact between adjacent coils when these slackened after constant use. The silica tube was held by spring clips at top and bottom onto Sindanyo board bracketed vertically onto the work-bench.

Measurement of the temperature rise induced in water flowing through this tube showed the heater to possess an efficiency of the order of sixty percent. Thus, sufficient power was available to raise the temperature of two litres of solution from room to working temperature in fifteen minutes. Control of temperature in the fluid circuit was achieved by "on-off" switching of the heater element through an amplifier-operated relay controlled by a "Tem-Con" thermostat.

This thermostat contains an expansion element in the stem which operates finely adjusted contacts in the head. The closing of these contacts raises the grid potential of the amplifier from which current then flows to energise a solenoid-operated relay. Sensitivity in this system is dependent upon the length of the expansion element and for this application a four inch stem, enclosed in a mercury filled glass sheath, proves adequate.

The original intention was to mount the thermostat in the specimen tank to ensure freedom from the influence of changes in ambient temperature. In practice, however, this proved unsatisfactory as vibrations transmitted from the fatigue machine caused the delicate contacts to "chatter". This was overcome by fitting the thermostat in a pyrex tube provided with inlet and outlet connections and attached firmly to the wall close to the specimen tank. It seemed possible that changes in room temperature would affect the temperature drop between thermostat and specimen tank but this effect proved

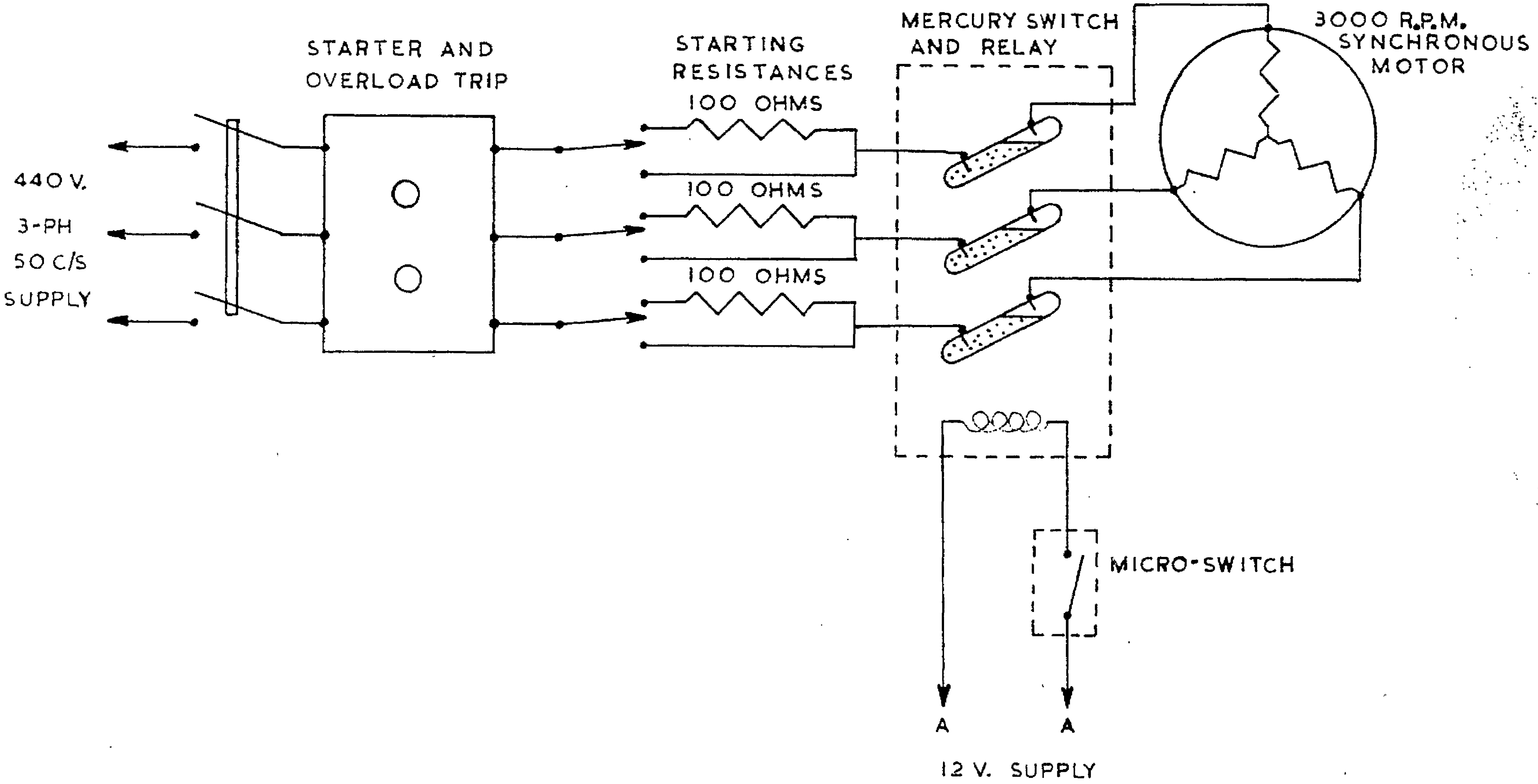


FIG. 6. FATIGUE TESTING MACHINE - WIRING DIAGRAM.

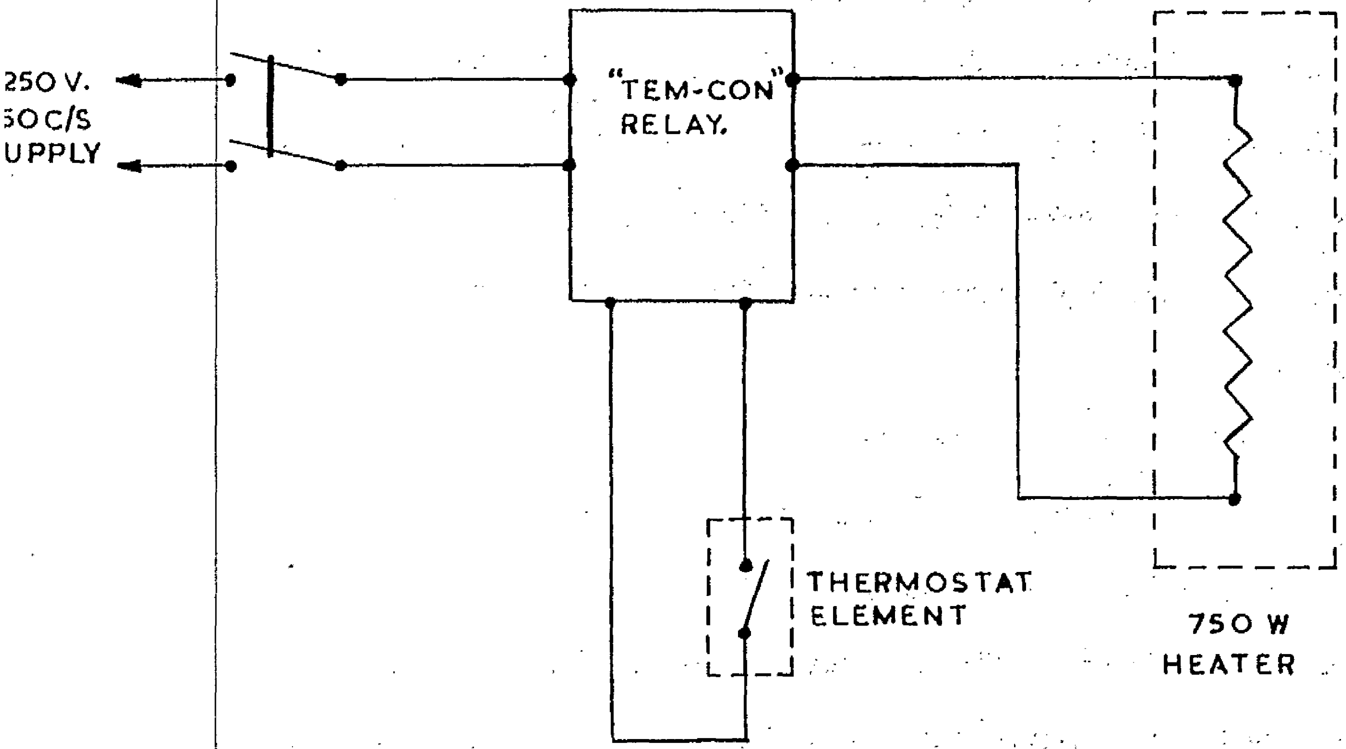


FIG.7. HEATER AND THERMOSTAT CIRCUIT-WIRING DIAGRAM

negligible and the temperature recorded by the specimen tank thermometer remained constant within ± 10° throughout the test.

Electrical Circuits.[1]

The electrical supplies required by the equipment comprise a 440-volt, three-phase, 50 cycles per second alternating current provided by a frequency-stable generator, and a 230-volt, single-phase alternating current from which a 12-volt supply is transformed. The application of these supplies is detailed in the wiring diagrams, Figures 6 and 7.

The need for a frequency-stable supply to the fatigue machine arises from the use of a synchronous motor, the speed of which is directly proportional to the supply frequency. Since the centrifugal force generated by the rotating head is proportional to the square of the motor speed it follows that a 2 percent variation in supply frequency would cause approximately a 4 per cent variation in the specimen load.

It may be seen from Figure 6 that line resistances have been incorporated in the supply to the fatigue motor. These were used during starting and served to reduce the acceleration of the motor from rest. It was found that without this reduction in starting torque the rotating head initially lagged behind the motor shaft due to the flexibility of the rubber coupling. As this lag was quickly overcome, however, the rotating head revolved for a few cycles at a speed much higher than the nominal 3000 r.p.m., causing the specimen to be overstressed during this period. This highly undesirable feature was removed by the use of the line resistances described, these being shunted out when steady running conditions had been achieved.

CHAPTER VII.

PREPARATION OF SPECIMENS AND SOLUTIONS.

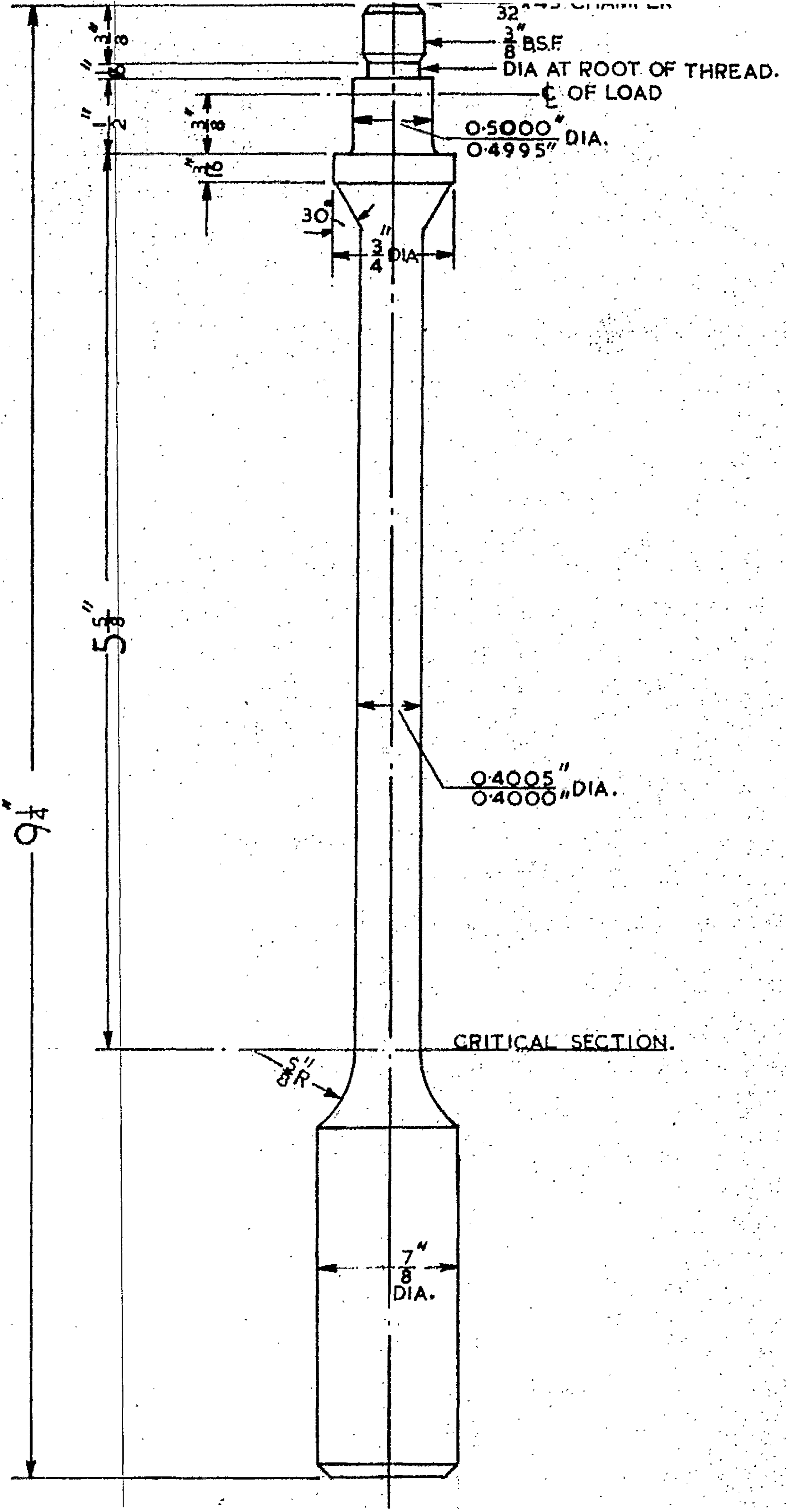


FIG. 8. CORROSION FATIGUE TESTPIECE.

Fatigue Specimen.

The fatigue specimens were machined from one-inch diameter annealed rolled bar. This bar came from one ingot so that a reasonable degree of uniformity in analysis and properties would result. The composition of the material and its tensile properties are detailed in Tables 1 and 2.

TABLE 1.

Composition of Specimen Material.

Element	Carbon	Silicon	Sulphur	Phosphorus	Manganese
Percentage	0.21	0.032	0.054	0.020	0.55

TABLE 2.

Tensile Properties of Specimen Material.

Yield point (Tons/sq.in.)	17.9
Maximum Stress (Tons/sq.in.)	30.8
Elongation on $L = 4\sqrt{A}$ (%)	38.0
Reduction of Area (%)	59.0

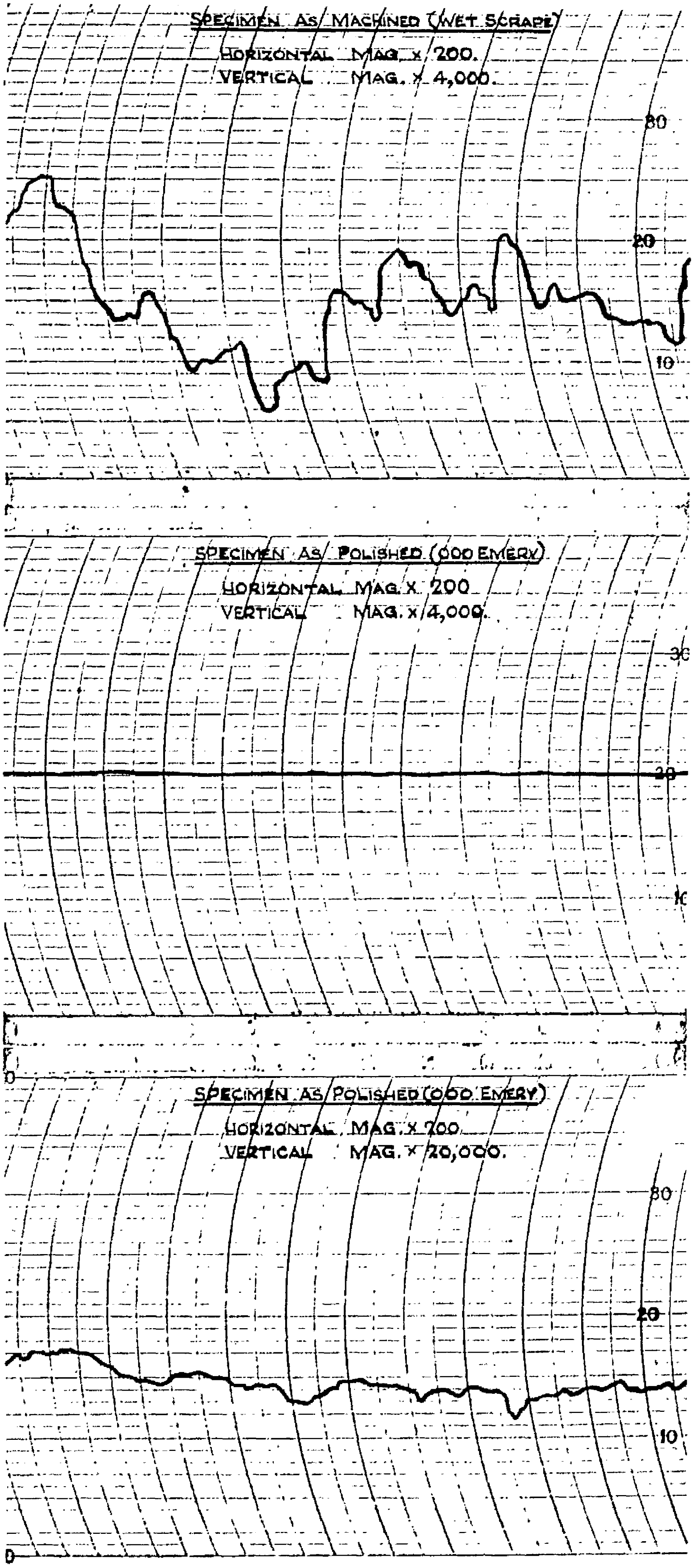


FIG. 9. INFLUENCE OF POLISHING ON SURFACE FINISH (REDUCED 2/3)

The form of the machined test-piece is illustrated in Figure 8. It may be seen that loaded as a cantilever where shown, the maximum tensile and compressive fibre stresses will be generated at the critical section where the parallel portion is radiused up to the shank diameter. The method of calculating the stress at this section will be detailed in the following Chapter.

The surface finish of the machined specimens was considered to be too coarse to produce consistent results and this was improved by careful hand polishing. The machine marks were first removed by polishing longitudinally with a coarse grade emery paper (1 G) followed by alternate circumferential and longitudinal polishing down to 000 emery, the scratches from the previous polishing being removed at each stage. The final polishing was carried out longitudinally so that minimum stress concentration would result under the applied stress system. The "Tallysurf" records reporduced in Figure 9 illustrate the improvement wrought by polishing, the final surface finish being regular to within 2.5 micro-inches.

Synthetic Sea-water.

Synthetic Sea-water.

To ensure consistency of composition over the experimental period, a synthetic sea-water to a composition recommended by the Chemical Research Laboratories, Teddington, was used throughout. Bulk supplies were made up from Analar reagents to the formula detailed in Table 3, and appropriate volumes were pipetted into a standard flask and diluted with distilled water to two litres to provide the concentration required for a particular test.

TABLE 3.

Composition of Synthetic Sea-water.

Constituent.	Gm. anhydrous salt/litre solution.
Sodium chloride.	27.26
Sodium bicarbonate.	0.11
Potassium chloride.	0.69
Potassium bromide.	0.09
Calcium sulphate.	1.29
Magnesium chloride.	3.51
Magnesium sulphate.	1.84

Inorganic Inhibitors.

To avoid repetitive weighing of very small quantities of solid inhibitors, these were stored in aqueous solutions of known strength. Thus, five percent by weight solutions of potassium dichromate, sodium chromate and potassium dihydrogen phosphate were made up from Analar reagents and test concentrations produced by dilution of appropriate volumes to two litres.

CHAPTER VIII.

EXPERIMENTAL PROCEDURE.

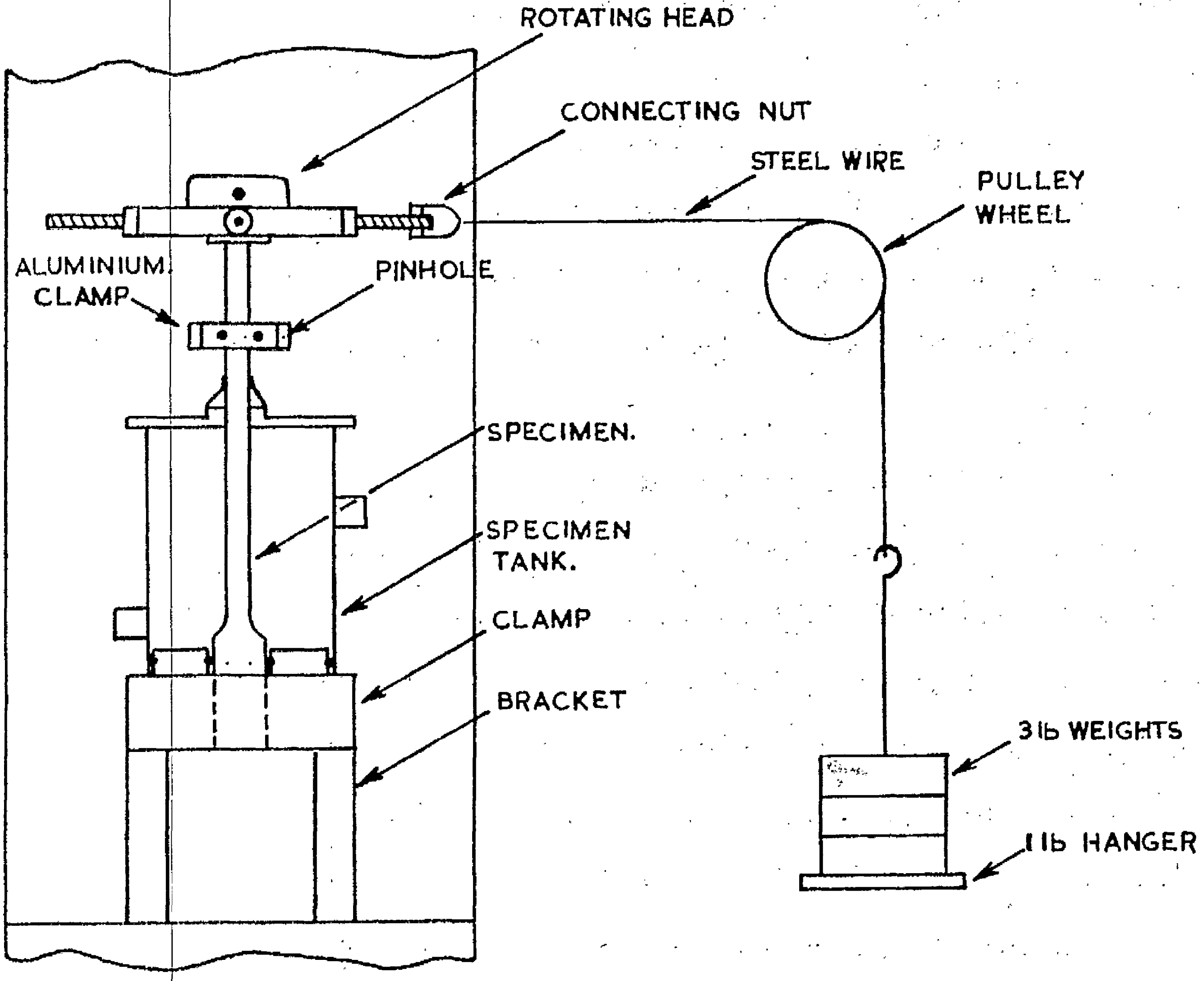


FIG.10. STATIC CALIBRATION SYSTEM

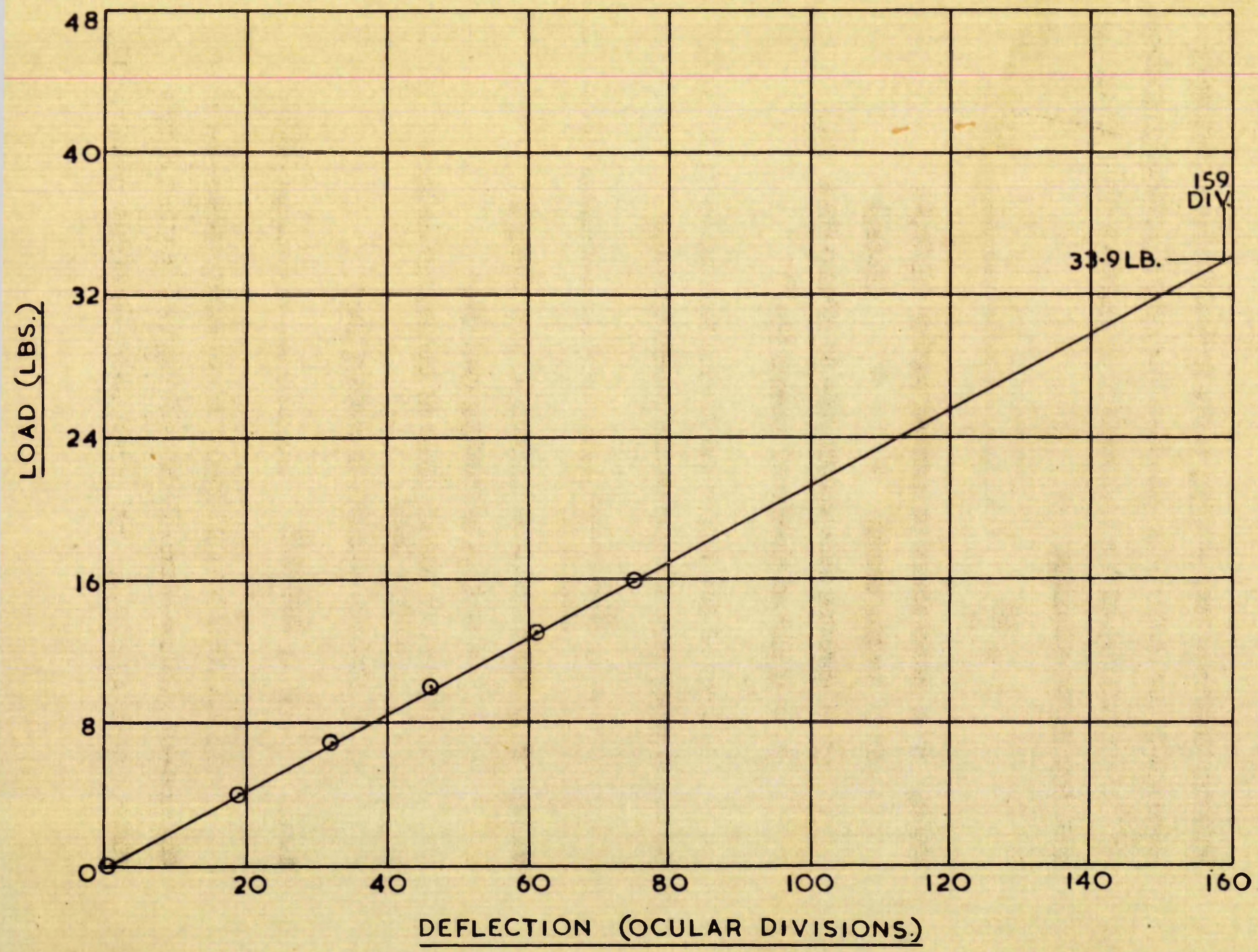
Calibration of Specimen.

The diameter of the parallel portion of the polished specimen above the critical section was first carefully measured by a micrometer. After thorough degreasing in acetone, the specimen was inserted through the base of the specimen tank, the cover placed in position and the membranous rubber seal affixed. This assembly was placed on the fatigue machine support bracket and the specimen shank rigidly clamped. The rotating head was next placed over the threaded end of the specimen and the inner ballrace held in position by tightening the capstan nut within the head.

The aluminium clamp containing the pinhole was then fixed to the specimen above the tank and aligned so that a fine light spot appeared in the centre of the microscope eyepiece. This light spot having been accurately focussed, its position was registered by moving the measuring shutter in the eyepiece until it formed a tangent to one side of the circular spot. The specimen was then statically calibrated using the device illustrated in Figure 10. Loads up to sixteen pounds weight were attached to the rotating head as shown and the resultant deflection of the specimen measured in ocular divisions by following the movement of the light spot with the shutter.

A typical plot of load versus deflection obtained by this method is included in Figure 11. It may be seen that a truly elastic proportionality has been obtained and the straight-line plot could be legitimately extrapolated to any load not exceeding the elastic limit.

FIG. II. TYPICAL LOAD-DEFLECTION CALIBRATION CURVE.



Thus the deflection corresponding to any desired load was obtained by reference to the static load-deflection graph for a particular specimen.

Calculation of the load required to produce a given stress was made from the relationship,

$$f = \frac{My}{I} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where, f = fibre stress at critical section (lb/in.^2)

M = bending moment " " (lb/in.)

y = distance from neutral axis to extreme fibre (in.)

I = Moment of inertia of section (in.^4)

In terms of the section and loading involved in the fatigue testing machine, this relationship may be restated as,

$$f = \frac{32\,W\ell}{2240\,\pi\,d^3} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where, f = fibre stress at critical section (T/in.^2)

W = load applied by rotating head (lb.)

ℓ = distance between point of loading and critical section (in.)

d = diameter at critical section (in.)

i.e.,

$$f = \frac{0.0228\,W}{d^3} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

By insertion into Equation 3 of the desired stress value and the measured specimen diameter, the load required to produce this stress can be calculated. The corresponding deflection obtained from the load-deflection graph may then be used to estimate the width of the light band produced in the microscope eyepiece when the desired stress is produced dynamically. Thus, this width will be twice the static deflection plus the spot diameter where these are expressed in ocular divisions.

e.g., If, required cyclic stress = ± 12.0 T/in.^{2}

specimen diameter = 0.4003 in.

light spot diameter = 52 divisions.

Then,

$$W = \frac{f\,d^3}{0.0228}$$

$$= \frac{12 \times (0.4003)^3}{0.0228} \text{ lb.}$$

$$= \underline{\underline{33.9 \text{ lb.}}}$$

Corresponding semi-deflection = 159 divisions (see Fig.11)

Thus, total bandwidth = (2 x 159) + 52 divisions.

= <u>370 divisions.</u>

Having determined the requisite bandwidth the out-of-balance weights on the rotating head were adjusted until the desired deflection was produced when the motor was running at 3,000 r.p.m. Since the specimen diameter varied and the positioning of the aluminium clamp was not exactly reproducible from test to test, it was essential to carry out the calibration procedure for every test. In practice, minor adjustments of the weights were needed to produce identical stresses in successive specimens. When final adjustment of the load had been made, the fatigue motor was switched off and attention directed to preparing the corrosive environment in which the fatigue test was to be run.

The fluid circuit.

Appropriate volumes of synthetic sea-water and inhibitor solution were pipetted into a standard flask and diluted to two litres with distilled water. After shaking thoroughly, this solution was transferred into the reservoir tank and the circuit completed, the specimen tank being by-passed at this stage. The pump was primed by allowing air to bleed from the outlet connection before the pump motor and heater were switched on, and the solution allowed to circulate until operation of the pre-set thermostat indicated that the required temperature had been attained. Pump motor and heater were then switched off, the fluid circuit connected through the specimen tank, and circulation restarted.

The initial flow through the specimen tank resulted, on occasion, in a few air bubbles attaching themselves to the specimen surface and these were immediately removed by successive stopping and starting of the pump motor which caused the solution to surge. It was found that if these bubbles were not removed they influenced the nature of the corrosive attack upon the specimen.

With the test solution circulating past the fatigue specimen at the correct temperature, the revolution counter was set at zero and the fatigue motor switched on through the starter resistances. The deflection of the specimen was again checked by measurement of the width of the light band in the microscope eyepiece, and the microswitch adjusted so that an increase of fifty percent in the specimen deflection would trip the motor relay.

During the course of the test periodic checks of solution temperature and specimen deflection were made and where necessary, the composition of the corrosive solution was determined by sampling and titration. In the case of distilled water environments, the only adjustments required during test were daily additions of up to 100 c.c. of water to restore the volume of the system to two litres. These additions were made to the reservoir tank without interruption of the test by partial removal of the inlet tube.

For tests run in sea-water, however, the combined effects of leakage and evaporation were best overcome by complete replacement of the fluid system with fresh preheated solution at twenty-four hour intervals. This required that the test be interrupted while the exchange was made, but the time involved was less than ten minutes and this was not considered sensibly to influence the life of the specimen. Titration of the old solution against decinormal silver nitrate showed the concentration caused by evaporation always to be less than two percent.

When inhibitors were added to the corrosive environment, alterations in composition could result from chemical reaction with the specimen surface, this effect being in the opposite sense to the concentration resulting from evaporation. Complete replacement of the solution each day was again found to be sufficient to maintain constancy of composition to within two percent.

The test was completed when the specimen failed or when it survived an arbitrary number of stress reversals (in this case 50 million). After the specimen had been removed, the system was drained of solution and flushed several times with hot distilled water preparatory to the ensuing test.

PART III.

PRESENTATION AND DISCUSSION OF RESULTS.

CHAPTER IX.

EXPERIMENTAL RESULTS.

Fatigue in Air.

To establish the time fatigue limit for the material, fatigue tests in air were carried out on the rotating-load fatigue machine at room temperature. The results of these tests are presented in Table 4.

TABLE 4.

Fatigue results for 0.21% Carbon Steel
in air at room temperature.

Specimen Reference.	Stress ± tons/in.^{2}	Cycles to failure (x 10^6)
A1	19.4	0.024
A2	16.0	0.286
A3	15.7	0.434
A4	15.5	0.521
A5	15.0	0.807
A6	14.6	1.52
A7	14.5	3.75
A8	14.5	Unbroken at 10.0
A9	14.3	Unbroken at 10.0
A10	13.8	Unbroken at 10.0

Corrosion Fatigue in Distilled Water.

Tests in distilled water at 88°C were carried out to determine the influence of aerated water on the fatigue characteristics of the specimen material. Table 5 shows the results obtained.

TABLE 5.

Corrosion Fatigue Results from 0.21% Carbon
Steel in aerated distilled water at 88°C.

Specimen Reference	Stress $\pm$ tons/in.^{2}	Cycles to failure ($\times 10^6$)
B1	14.6	0.93
B2	12.8	4.13
B3	12.7	4.58
B4	12.5	6.00
B5	11.5	29.72
B6	10.9	49.24
B7	10.3	Unbroken at 50.0

Corrosion Fatigue in Synthetic Sea-water.

An investigation was made of the influence of solution concentration on the severity of corrosion fatigue at 88°C. Stress-endurance values for the specimen material were derived for varying concentrations of synthetic sea-water. The results are tabulated under Table 6.

TABLE 6.

Corrosion fatigue results for 0.21% Carbon steel in aerated synthetic sea-water of various concentrations at 88°C.

Specimen Reference.	Sea-water Concentration.	Stress ± tons/in^2	Cycles to failure (x 10^6)
C1	2.5%	14.0	1.32
C2	"	12.0	2.33
C3	"	11.2	5.90
C4	"	9.2	9.82
C5	"	7.7	17.41
C6	"	7.1	25.40
C7	"	5.2	40.80
C8	"	4.3	Unbroken at 50.0
C9	5.0%	14.0	0.97
C10	"	12.0	3.24
C11	"	9.0	11.73
C12	"	6.7	20.49
C13	"	4.7	32.40
C14	"	2.8	Unbroken at 50.0
C15	10.0%	14.0	0.81
C16	"	12.0	2.85
C17	"	9.3	10.27
C18	"	7.2	14.45
C19	"	5.4	24.47
C20	"	3.1	38.20
C21	"	2.2	Unbroken at 50.0

The effect of inhibitors on corrosion fatigue.

A complete study of the effects of inhibitors at various concentrations on the corrosion fatigue characteristic of the material in several concentrations of sea-water would have involved some hundreds of tests. Accordingly, to obtain information in the time available, it was decided to determine their effect at a selected stress value. In order to assess the value of stress to be used, an initial survey was made of the stress-endurance characteristic of the material in 2.5 percent sea-water containing an added 500 parts per million of potassium dichromate. The results are included in Table 7.

TABLE 7.

Corrosion fatigue results for 0.21% Carbon Steel in 2.5% synthetic sea-water containing 500 p.p.m. potassium dichromate at 88°C.

Specimen Reference.	Stress ± tons/in².	Cycles to failure ($\times 10^6$)
D1	7.3	Unbroken at 50.0
D2	8.0	Unbroken at 50.0
D3	10.8	16.40
D4	11.6	9.54
D5	12.0	2.63

Examination of these results suggested that, if higher inhibitor concentrations were to be tested, it would be advisable to conduct the experiments at high values of stress so that the endurances recorded would fall within 50 x 10^6 cycles. The effects of inhibition would be totally masked, however, if the stress were to exceed the fatigue limit in air, and accordingly the remainder of the inhibitor tests were conducted at ± 12.0 Tons/ins.

The influence of potassium dichromate additions on specimen life is illustrated by the results given in Table 8.

TABLE 8.

Endurance of 0.21% Carbon Steel at ± 12 Tons/in^2
in synthetic sea-water containing potassium dichromate
at 88°C.

Specimen Reference.	Sea-water Concentration	$K_2Cr_2O_7$ Concentration	Cycles to failure ($\times 10^6$)
D5	2.5%	0.05%	2.63
D6	"	0.10%	5.49
D7	"	0.15%	3.96
D8	"	0.20%	5.91

Table 9 presents the results obtained when the effects of sodium chromate as an inhibitor were studied. The long endurances recorded in 2.5% synthetic sea-water at small chromate concentrations encouraged the examination of their effects in 5.0% sea-water.

TABLE 9.

Endurance of 0.21% Carbon steel at ±12 Tons/in^2 in synthetic sea-water containing sodium chromate, at 88 °C.

Specimen Reference	Sea-water Concentration.	$NaCrO_4$ Concentration	Cycles to failure (x 10^6)
E1	2.5%	0.025%	7.93
E2	"	0.05%	39.2
E3	"	0.10%	Unbroken at 50.0
E4	5.0%	0.05%	8.45
E5	"	0.10%	10.7
E6	"	0.20%	25.4
E7	"	0.30%	Unbroken at 50.0
E8	"	0.40%	Unbroken at 50.0

The success achieved by Palmer(44) in inhibiting stressless corrosion of steel in chloride solutions by additions of a phosphate-dichromate mixture, suggested that such a mixture should be tried under corrosion fatigue conditions. A ratio of two parts potassium dihydrogen phosphate to one part potassium dichromate was used and the results obtained in 2.5% and 5% sea-water are given in Table 10.

TABLE 10.

TABLE 10.

Endurance of 0.21 Carbon steel at ± 12 Tons/in^2 in synthetic sea-water containing phosphate-chromate mixture at 88°C.

Specimen Reference	Sea-water Concentration	KH_2PO_4 Concentration	$K_2Cr_2O_7$ Concentration	Cycles to failure ($\times 10^6$)
F1	2.5%	0.10%	0.05%	10.2
F2	"	0.20%	0.10%	Unbroken at 50.
F3	5.0%	0.10%	0.05%	4.54
F4	"	0.20%	0.10%	18.8
F5	"	0.30%	0.15%	42.3
F6	"	0.40%	0.20%	Unbroken at 50.0

CHAPTER X.

METALLOGRAPHIC FEATURES OF CORROSION FATIGUE.

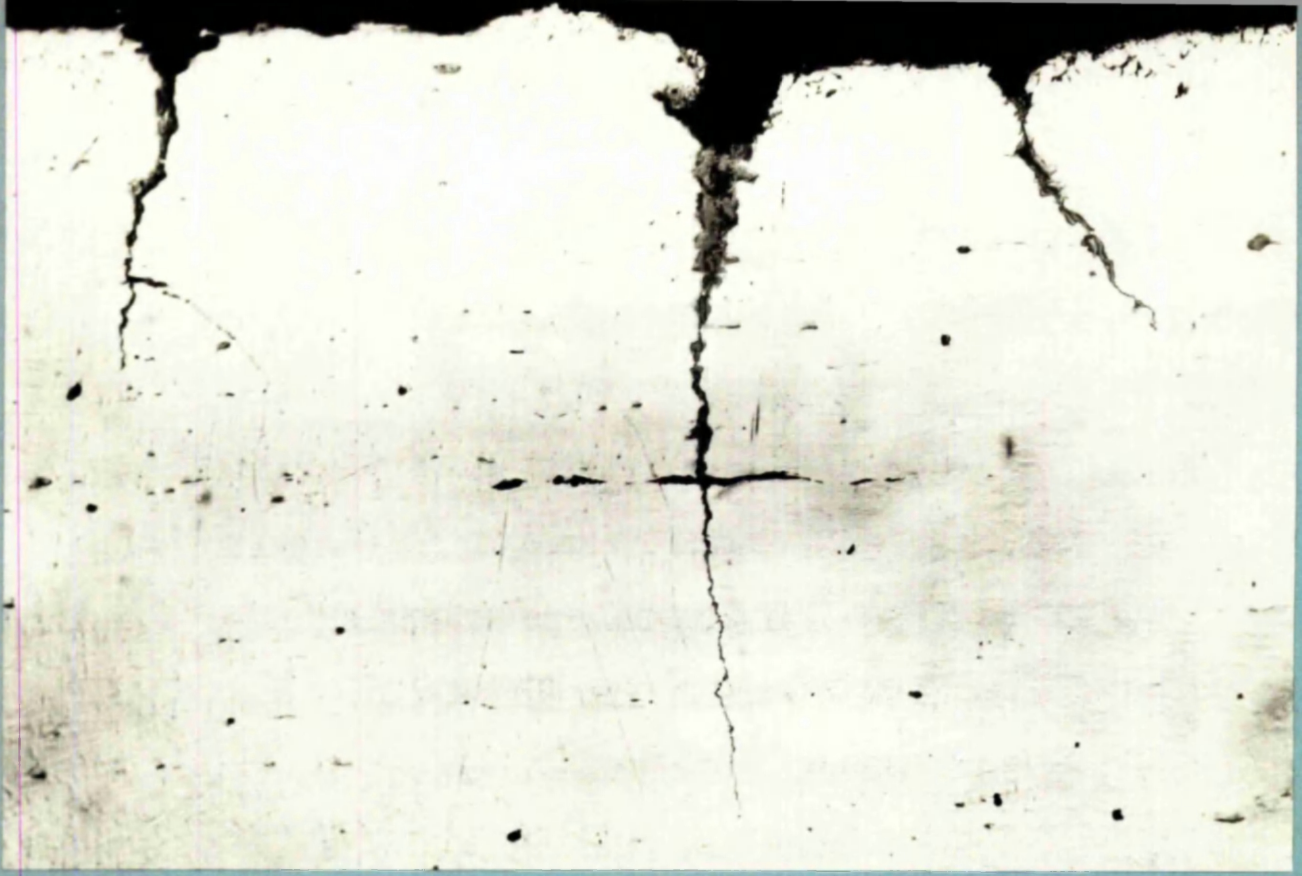


PLATE 5. CORROSION FATIGUE CRACKS SHOWING DIVERGENT PATHS (x 70)

PLATE 6. CORROSION FATIGUE CRACKS IN VARIOUS STAGES OF DEVELOPMENT (x 7

During the investigation, a number of tested specimens were sectioned, polished and subjected to microscopic examination. The most informative sections were found to be those taken longitudinally down the specimen axis, since such sections cut perpendicularly through the planes along which the corrosion fatigue cracks developed.

Typical examples of the appearance of such sections are presented in Plates 5(x70) and 6(x70) which show diametrically opposite edges of specimen G13 at a region immediately above the plane of failure. This specimen had fractured after 32.4 x 10^6 cycles of stress at ± 4.7 tons/sq.in. in 5.0 percent sea-water at 88°C. When it is considered that this section represents only one of the many which might have been taken, it can be appreciated that the total number of corrosion fatigue cracks in various stages of development contained in this specimen is very large indeed.

An interesting feature of Plate 5 is the divergence of the two lesser cracks from the principal crack in the centre. This tendency to veer away from the principal crack suggests that this crack has developed first, and so modified the stress pattern in the immediate neighbourhood that subsequently developing cracks have diverged in order to propagate in directions perpendicular to the lines of maximum stress. A similar effect can be observed in Plate 6.

The principal crack shown in Plate 5 passes through a large non-metallic inclusion approximately halfway along its length and this

PLATE 7. CORROSION FATIGUE CRACK TRAVERSING INCLUSION (x 500)

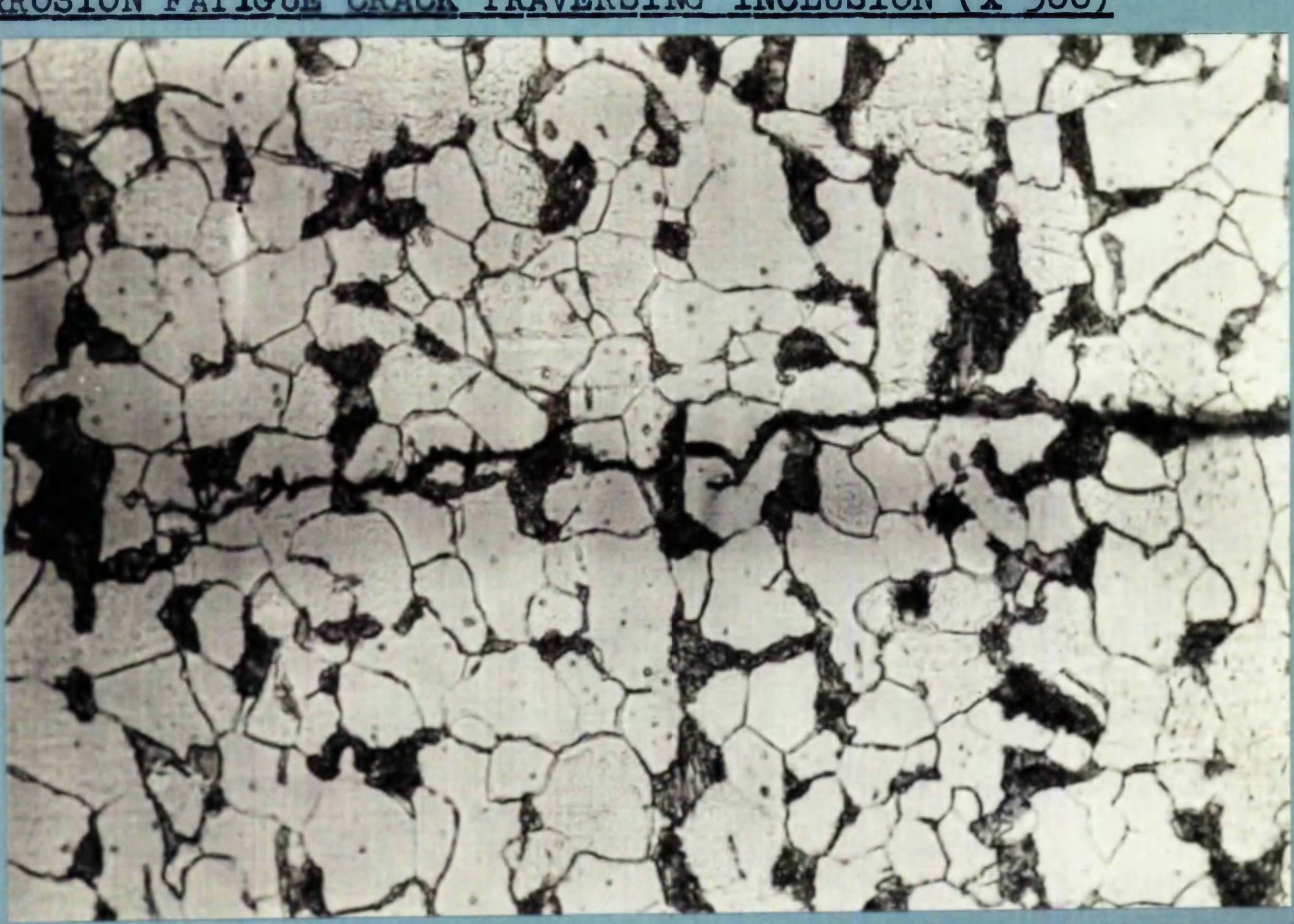


PLATE 8. CORROSION FATIGUE CRACK SHOWING TRANSCRYSTALLINE PATH (x 500)

region is shown at higher magnification in Plate 7 (x500), where the inclusion may be recognised at the right-hand side of the photomicrograph.

Careful inspection shows that the crack narrows perceptibly where it passes through the inclusion and opens out again on the left-hand side. It is clear that the inclusion itself has suffered no chemical attack but has cracked solely due to the fatigue stresses to which it has been exposed when the crack front has reached it.

Plate 8 (x500) shows the tail-end of the principal crack in Plate 6 at a higher magnification. From this it can be seen that the crack path is truly transcrystalline as would be found in simple fatigue. Although the general direction of crack propagation is perpendicular to the axis of the specimen, it is evident that local deviations can occur from grain to grain. This is in agreement with Gough and Sopwith's(26) observation that corrosion fatigue cracks propagated within a crystal in a direction parallel to the traces of operative slip planes. An interesting feature of this mechanism is that the crack direction may alter within a grain, an example of this being evident in the centre of Plate 8. This is presumably the result of two sets of slip planes within the grain having been so disposed as to share the total slip deformation in almost equal measure.

Inspection of the crack width as evident in Plates 5 to 8, shows that in general this decreases with increasing penetration. The contrasting appearance of a simple fatigue crack is shown in Plate 9 (x500) where the transcrystalline crack maintains a uniform width along its length. The

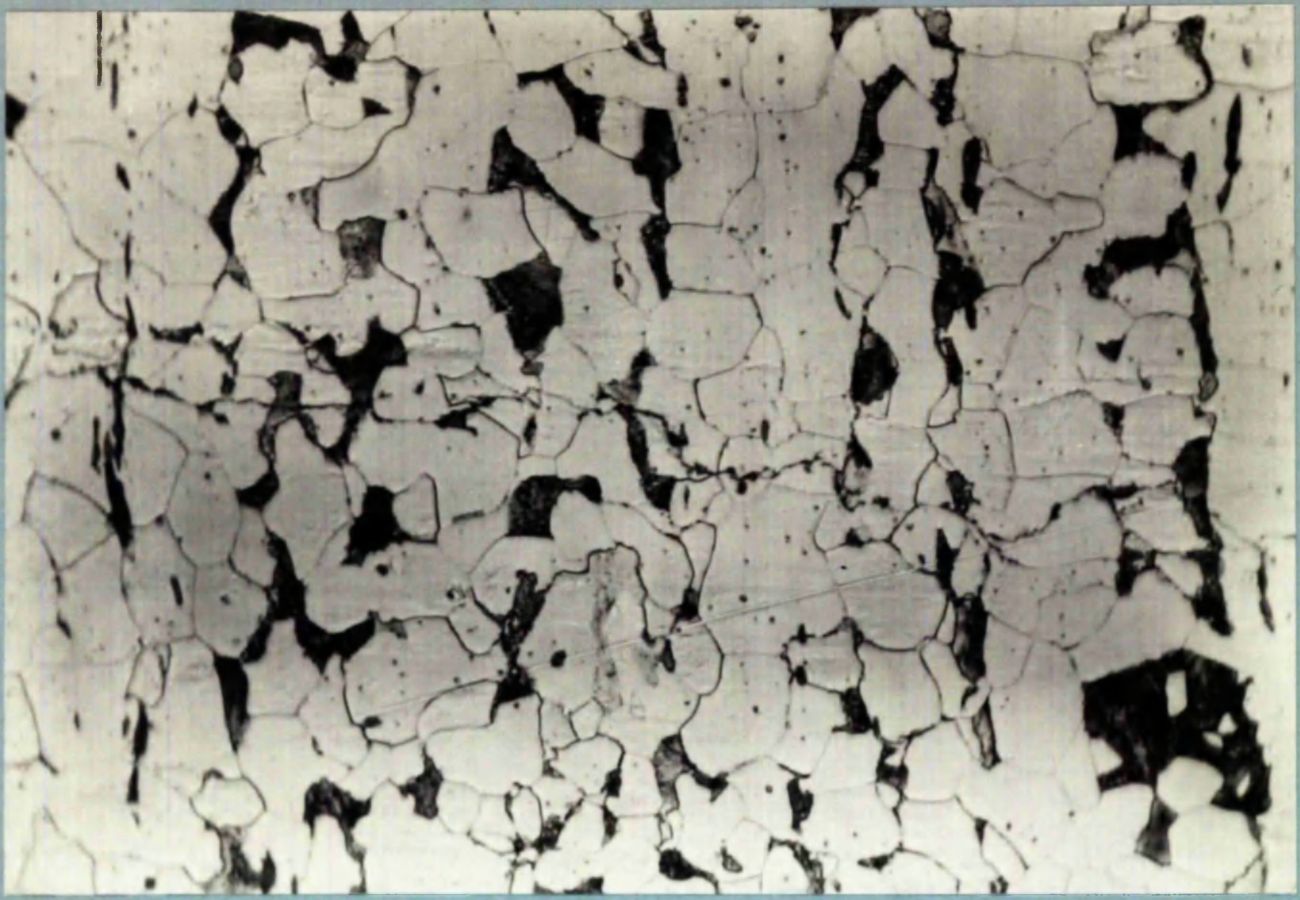


PLATE 9. SIMPLE FATIGUE CRACK (x 500)

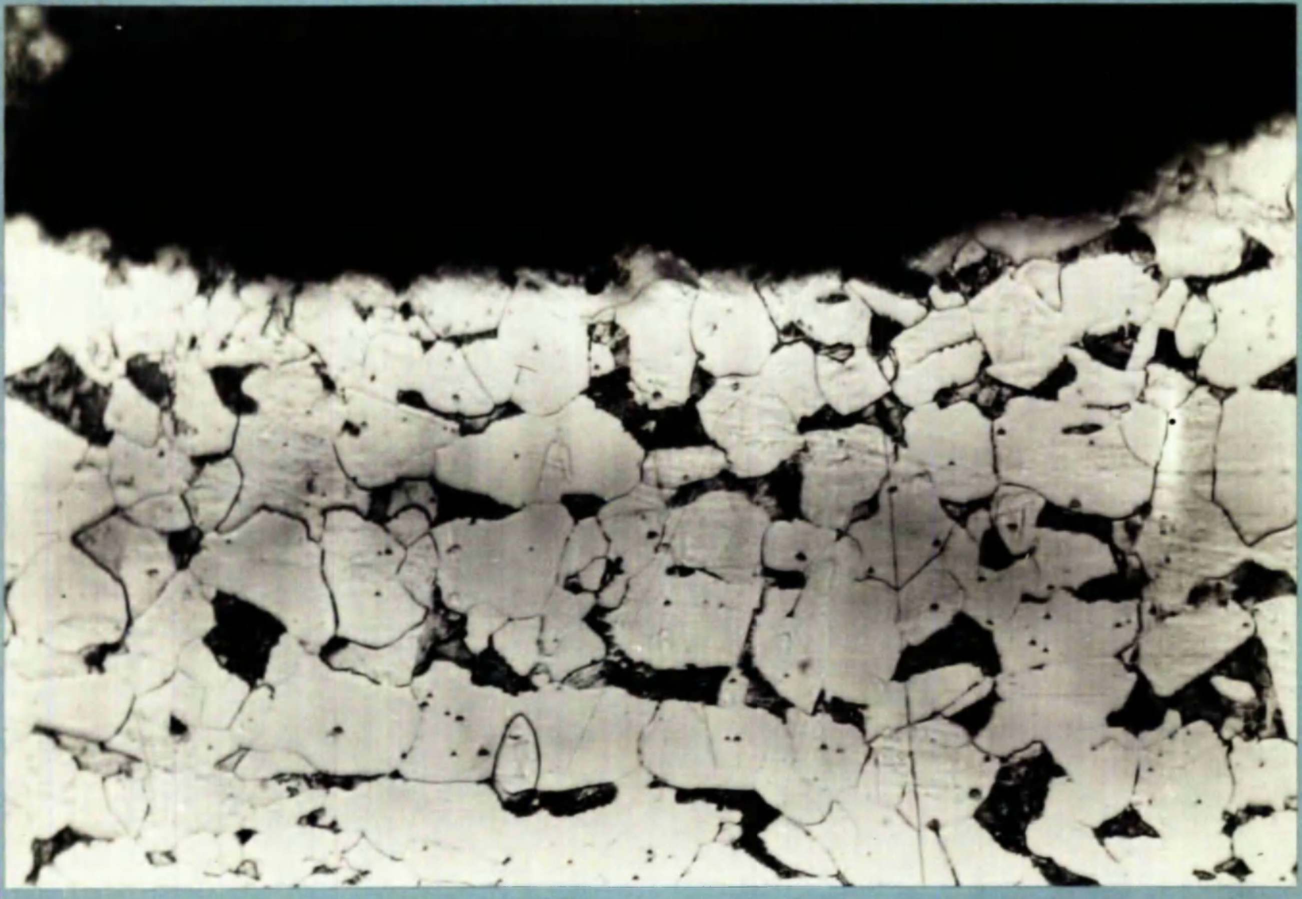


PLATE 10. SIMPLE CORROSION PIT (x 500)

difference is almost certainly due to the corrosion of the crack walls following the advance of the crack front in the case of corrosion fatigue. Such secondary corrosion of the crack walls would require some considerable time to develop since the accelerating influence of stress would be absent after the crack front has advanced. This suggests that the rate of propagation of a corrosion fatigue crack is of a much lower order than that of a simple fatigue crack.

In contrast to the crevice-like pits from which corrosion fatigue cracks develop, Plate 10(x500) illustrates the appearance of a section through a specimen which had been subjected only to corrosion in 5.0 percent sea-water for 7 days (equivalent to 30 x 10^6 cycles at 3000 c.p.m.) The saucer-shaped pit is typical of simple corrosion where the accelerating and directional influence of cyclic stress is absent.

It will be shown in the following Chapter (page 80) that the presence of potassium dichromate in dilute sea-water radically reduces the number of pits which develop on a fatigue specimen surface. An insight into the action of the inhibitor is provided by the section illustrated in Plate 11 (x70). In this case, the specimen was stressed at 10.8 tons-sq.in. in 2.5 percent sea-water containing 0.05 percent potassium dichromate giving an endurance of 16.4 x 10^6 cycles. The overall length of the crack in Plate 11 is equal to 85 percent of the specimen diameter. Distinctive features of this crack are the sharpness of the crevice from which it has developed and the smooth edge to this crevice as compared with equivalent regions in Plates 5 and 6.

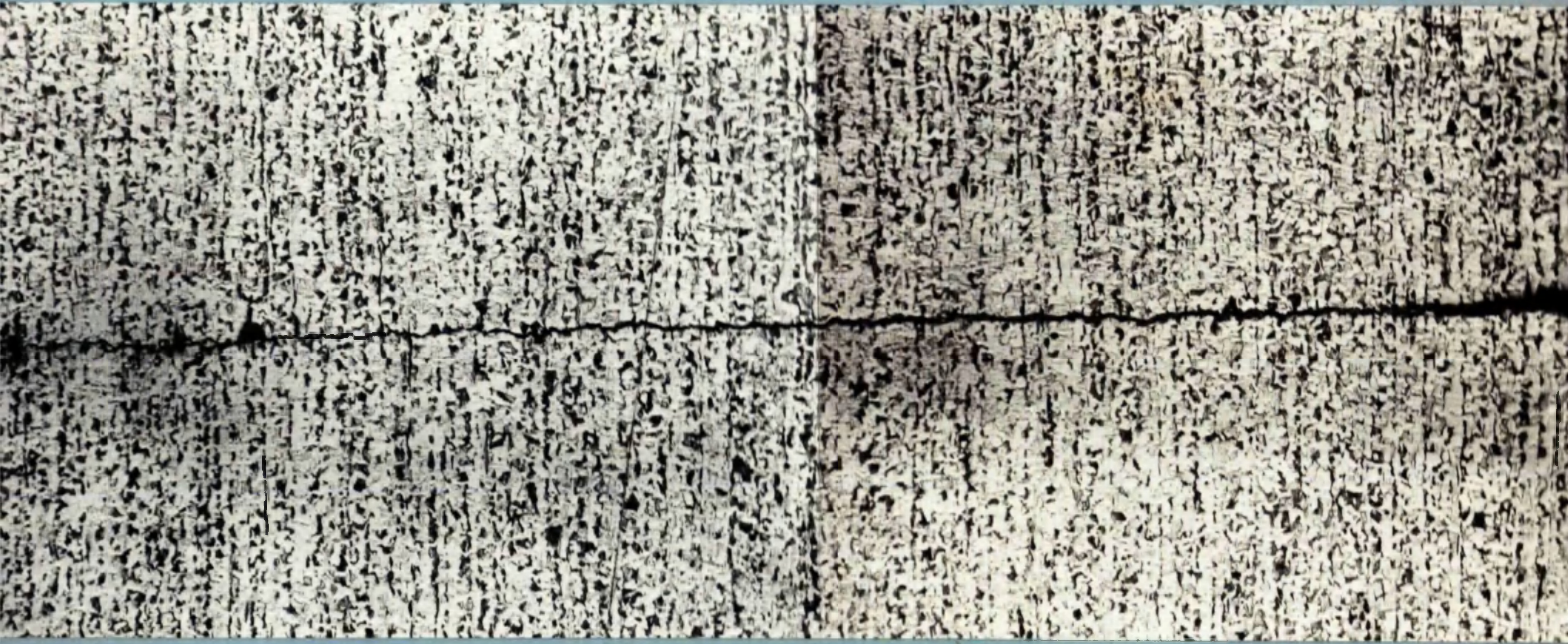


PLATE 11. MAJOR CORROSION FATIGUE CRACK (x 70)

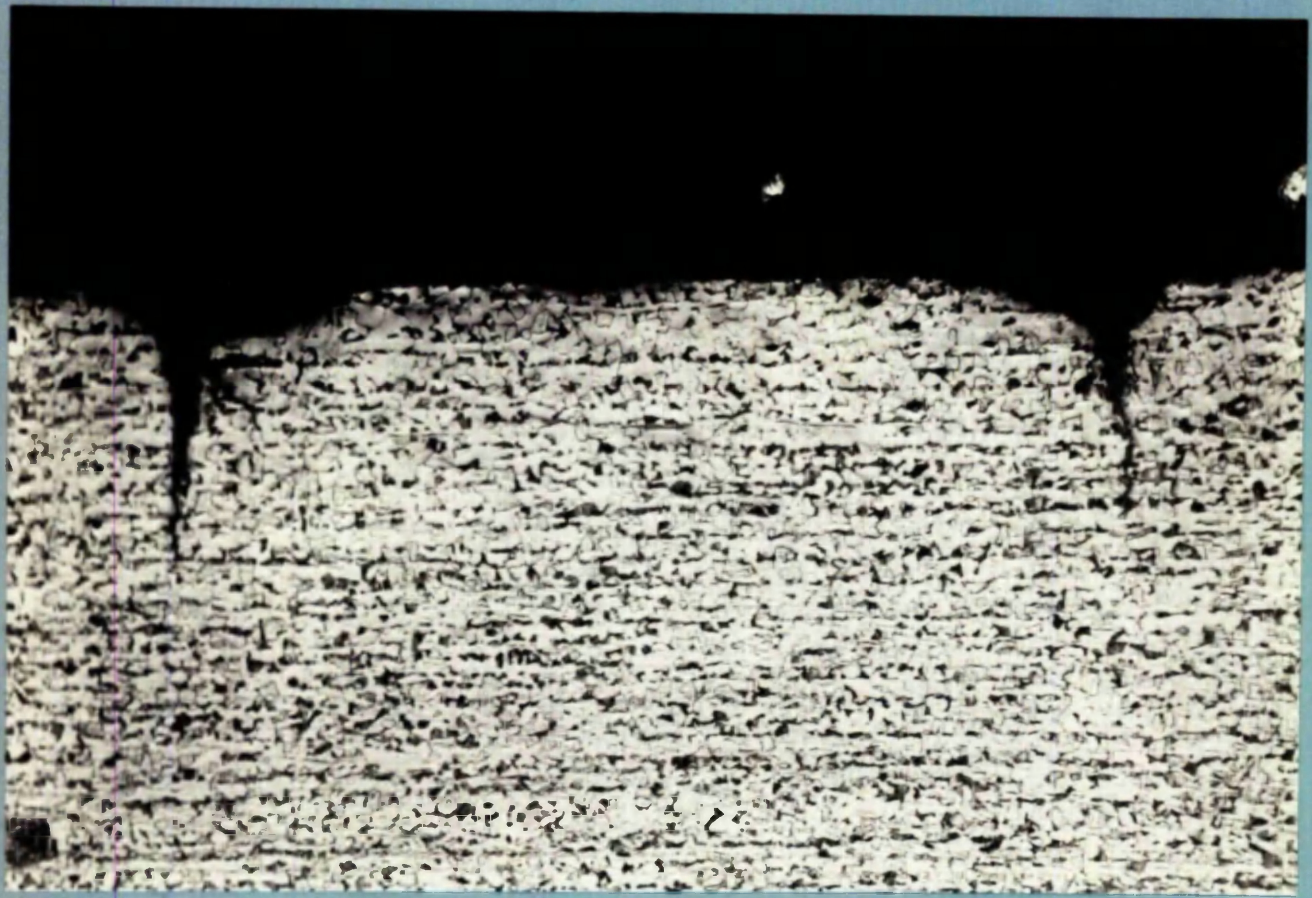


PLATE 12. UNDEVELOPED CORROSION FATIGUE PITS (x 70)

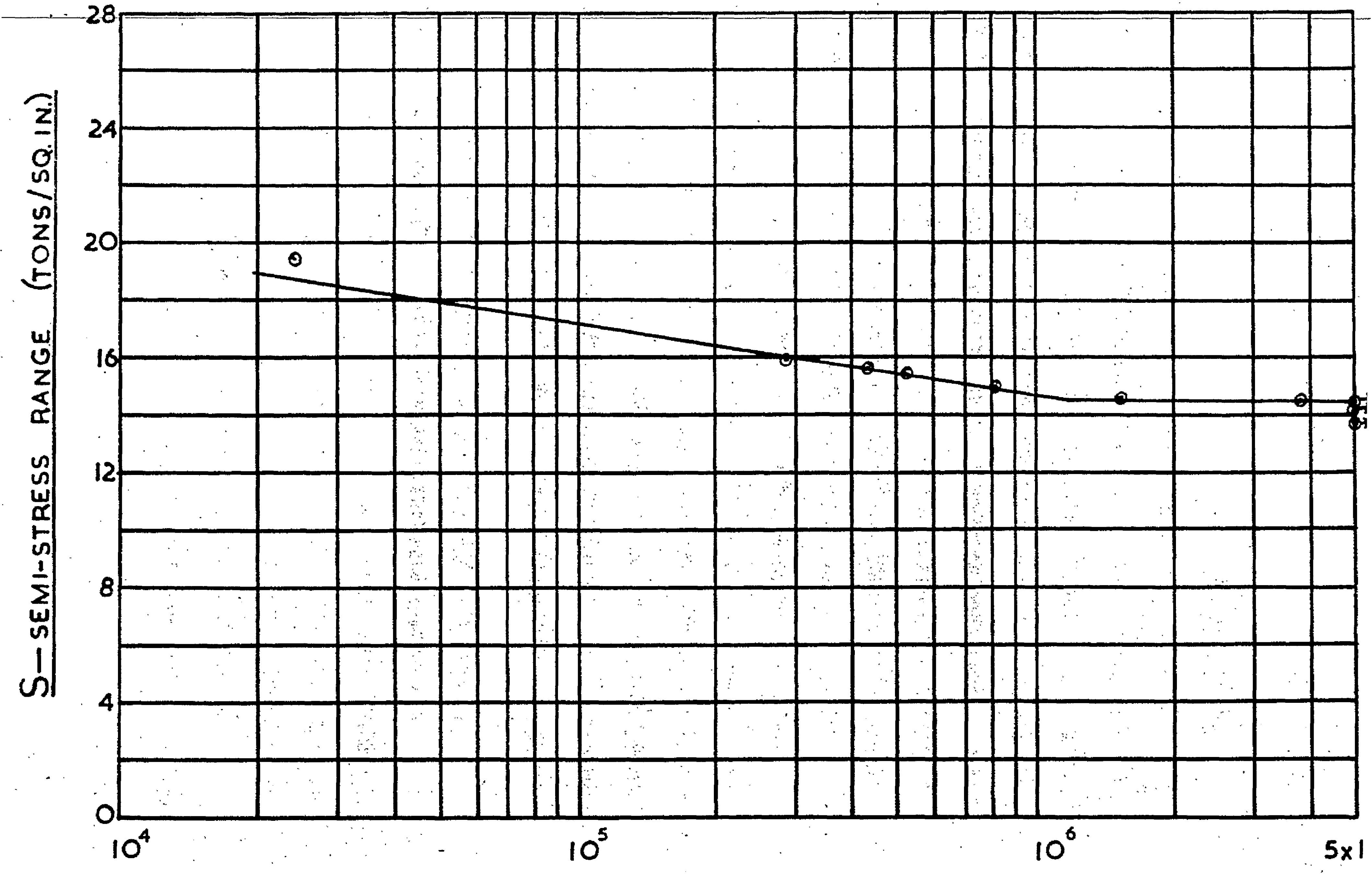
These features are repeated in Plate 12 (x70) which shows, for the same specimen, two crevices which have not developed into corrosion fatigue cracks proper, and they suggest that the secondary corrosion of the crack walls previously postulated is largely suppressed by the presence of the inhibitor. It seems likely, then, that in addition to restricting the number of points on the specimen surface which are actively pitted by corrosion, the inhibitor has reduced the number of such pits which can initiate corrosion fatigue cracks. This increased selectivity has produced a situation akin to simple fatigue where failure commonly occurs from the propagation of very few cracks.

CHAPTER XI.

DISCUSSION OF EXPERIMENTAL RESULTS.

FIG. 12. S-LOGN CURVE FOR 0·2% C STEEL TESTED IN AIR AT 18°C.

TEST FREQUENCY 3000 C.P.M.
POINTS THUS ⊙→ DENOTE SPECIMEN UNBROKEN.



Fatigue in Air.

The results included in Table 4 are graphed to axes of stress and endurance in Fig.12, where the established practice of expressing endurance as a logarithmic function has been followed. The curve obtained shows a clearly established fatigue limit of ±14.5 tons-sq.in. The ultimate tensile stress of this 0.21% Carbon steel in the annealed condition is 30.8 tons/sq.in., so that the ratio of fatigue limit to ultimate tensile stress is 0.47.

This is in good agreement with the data presented by Cazaud(57) who found, in a comprehensive survey of the fatigue properties of carbon steel, that this ratio varied between 0.26 and 0.59 according to the composition and heat treatment of the material. For a 0.19% carbon steel in the annealed condition, however, he quotes a ratio value of 0.48. An identical ratio value may be derived from examination of Gould's(23) figures obtained on a 0.15% carbon steel.

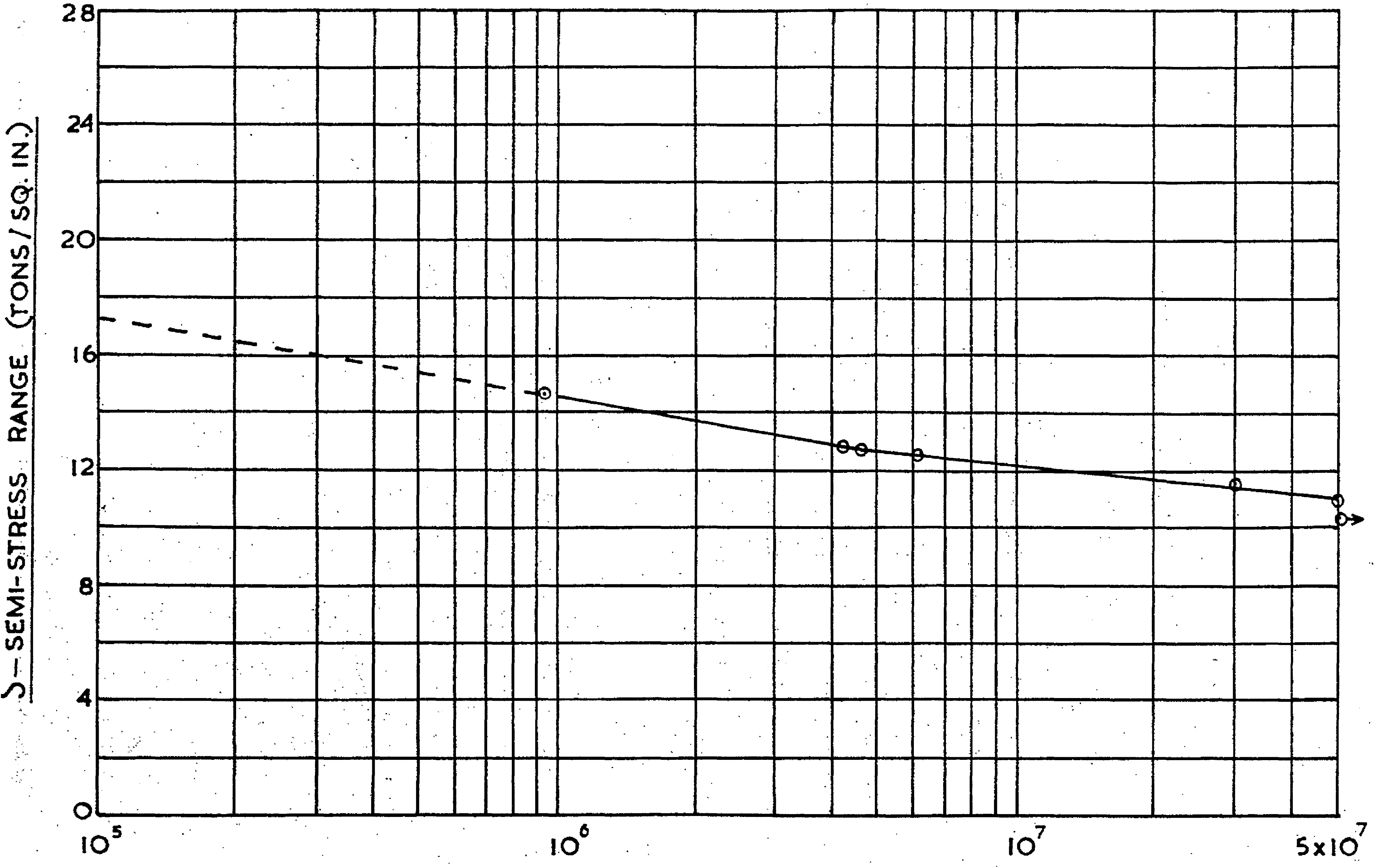
Corrosion fatigue in aerated distilled water at 88°C.

The stress-endurance characteristic for the material in aerated distilled water at 88°C is presented in Fig.13. Examination of this reveals no evidence of a true corrosion fatigue limit at endurances up to 50×10^6 cycles.

As the range of cyclic stress is reduced, the specimen endurance increases exponentially according to the general equation, $N = e^{kS}$,

FIG. 13. S-LOGN CURVE FOR 0·2%C. STEEL IN DISTILLED WATER AT 88°C.

TEST FREQUENCY 3000 C.P.M.
POINT THUS ⊙→ DENOTES SPECIMEN UNBROKEN



where N = endurance in cycles.
S = semi-range of stress.
k = constant.

The value of k, however, does not appear to be truly constant over the entire range of endurances studied and a change in the slope of the S/Log.N curve at S = 12.7 tons/sq.in. is indicated by Fig.12.

Comparison of the endurance limits at various numbers of reversals with those obtained by Lehman(53), Gould(23) and Karpenko(32) for similar materials in distilled water is made in Table 11. Differences in experimental conditions, particularly flow rate, temperature and frequency make correlation difficult but some general conclusions may be drawn from the comparison.

TABLE 11.

Investigator		Lehman(53)	Gould(23)	Karpenko(32)	Author
Steel		0.13% C.	0.15% C.	0.20% C. 1.0 % Cr.	0.21% C.
Fatigue limit in air(tons/sq.in.)		17.2	17.0	18.9	14.5
Test frequency. (c.p.m.)		2000		Not stated.	3000
Test temperature.		96°C	Room	Room	88°C
Endurance limit in distilled water (tons per sq.in.)	At 10×10^6	16.6	9.5	13.0	12.0
	At 20×10^6	-	-	12.1	11.8
	At 50x10	-	-	-	10.8

The high value of endurance limit at 10^7 cycles found by Lehman is almost certainly a consequence of the small amount of oxygen available in the specimen environment. His experimental technique exposed the specimen surface to the action of a small volume of water (approx. 12 c.c.) which remained unchanged throughout the test. The quantity of oxygen involved in the corrosion reaction was thus strictly limited and the high endurance limit obtained under such conditions is readily understood.

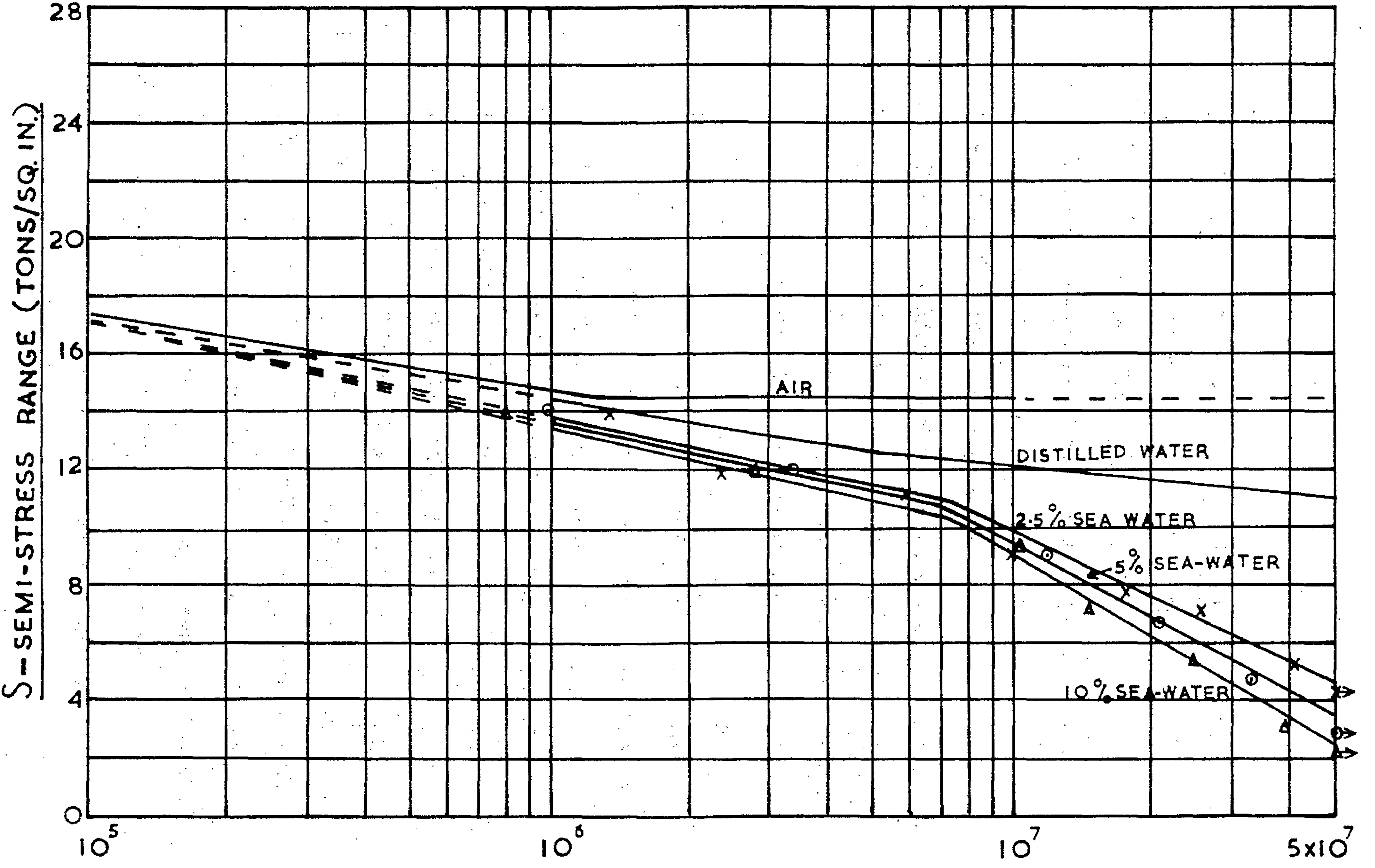
The very low value of endurance limit determined by Gould may be attributed to the inclusion of the results of tests where the specimens failed at the air-water interface. The exceptional severity of attack at such interface regions has been demonstrated by Evans(59) in the case of stressless corrosion and this effect might reasonably be expected to operate in the case of corrosion fatigue.

Karpenko's results on a 1% chromium steel illustrate the dependence of endurance limit upon the corrosion resistance of the material. Although the fatigue limit in air of this material is higher by 4.4 tons/sq.in. than that of the authors plain carbon steel, the differential under corrosion fatigue conditions is reduced to 1.0 tons/sq.in. at 10^7 cycles and to 0.3 tons/sq.in. at 2×10^7 cycles. Thus the superior fatigue strength of the 1% chromium steel in air is virtually eliminated by exposure to a corrosive environment.

FIG. 14. S-LOGN CURVES FOR 0·2%C STEEL IN SYNTHETIC SEA-WATER AT 88°C.

TEST FREQUENCY 3000 C.P.M.

POINTS THUS ⊙→ ×→ △→ DENOTE SPECIMENS UNBROKEN



Corrosion fatigue in aerated synthetic sea-water at 88°C.

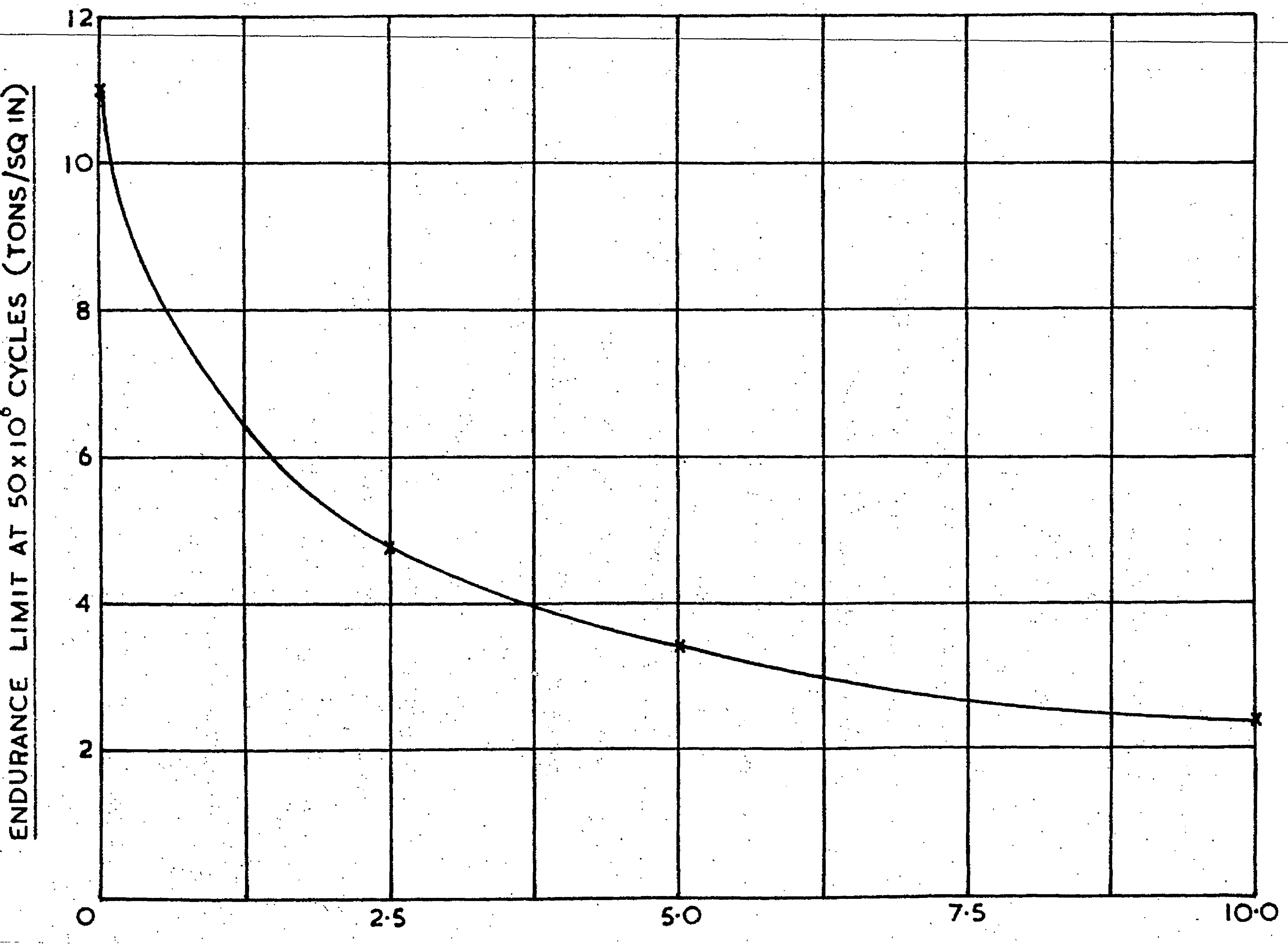
Fig.14 shows the stress-endurance curves obtained at sea-water concentrations of 2.5, 5.0 and 10.0 percent. The fatigue characteristics in air and in distilled water have been added to facilitate comparison.

The curves clearly illustrate the severe increase in corrosion fatigue attack resulting from relatively small additions of sea-water to the aqueous environment. The relation between the endurance limit at 50 x 10^6 cycles, derived from these curves, and sea-water concentration is presented in Fig.15, from which it is evident that the endurance limit decreases exponentially with increasing sea-water concentration. From the shape of the curve in Fig.15 it would be reasonable to predict that further addition of sea-water beyond 10 percent would cause little further fall in endurance limit.

An interesting feature of the stress-endurance characteristics in sea-water (Fig.14) is the sudden change of slope that occurs in all these curves at a cyclic stress in the range ±10.4 to ±11.0 tons/sq.in. Such a marked change of slope is highly suggestive of some radical change in the mechanism of failure at this stress level. By employing the concept of an effective stress concentration factor, characteristic of a corrosion fatigue crack in mild steel, the author has arrived at a satisfactory explanation of this feature of the S - Log.N curves and this is presented in the following argument.

The theoretical stress concentration factor associated with a notch in a specimen is that factor by which the nominal stress on the

FIG 15 ENDURANCE LIMIT AS A FUNCTION OF SEA-WATER CONCENTRATION



section would be raised by reason of the discontinuity in the surface if the material behaved in a truly elastic fashion under the applied stress. This factor may be calculated for simple geometrical notches using the classical theories of elasticity and is, by virtue of these considerations, independent of the plastic properties of the material.

In practice, however, plastic deformation at the root of the notch can effectively modify the elastic strain pattern and serve to reduce the peak value of stress attained. This ability to accommodate local stress peaks by plastic deformation is a material characteristic and varies widely from alloy to alloy, being reflected in the notch sensitivity of the material. The factor by which the nominal stress on a section is effectively raised in practice by a notch is termed the effective stress-concentration factor for that notch in the particular material under consideration.

By experimentally determining the endurance limits of notched and unnotched specimens of a specific material, a practical measure of the effective stress-concentration factor in fatigue may be obtained from the ratio of the endurance limit of unnotched material to the endurance limit of notched material.

We may consider the life of a corrosion fatigue specimen up to the point where final failure occurs to consist of three principal periods. During the first period, corrosion, accelerated by surface stress differentials, causes the formation of pits on the specimen surface. From the bases of these pits, fissure-like crevices develop during the second period extending in depth and increasing in sharpness until they become true corrosion fatigue cracks. When the stress-concentration at the crack front of one or more of these raises the stress level in a critical volume of material to a value somewhat above the true fatigue limit of the material, the third period mechanism of simple fatigue crack propagation comes into operation.

If, however, the effective stress-concentration factor for a corrosion fatigue crack tends to a low limiting value with increasing penetration, then it is evident that below some level of nominal stress the third period mechanism of simple fatigue will not operate, since the product of nominal stress x effective stress concentration factor will never reach the true fatigue limit of the material. Failure at such low stresses will thus occur only after a prolonged period of corrosion fatigue crack propagation.

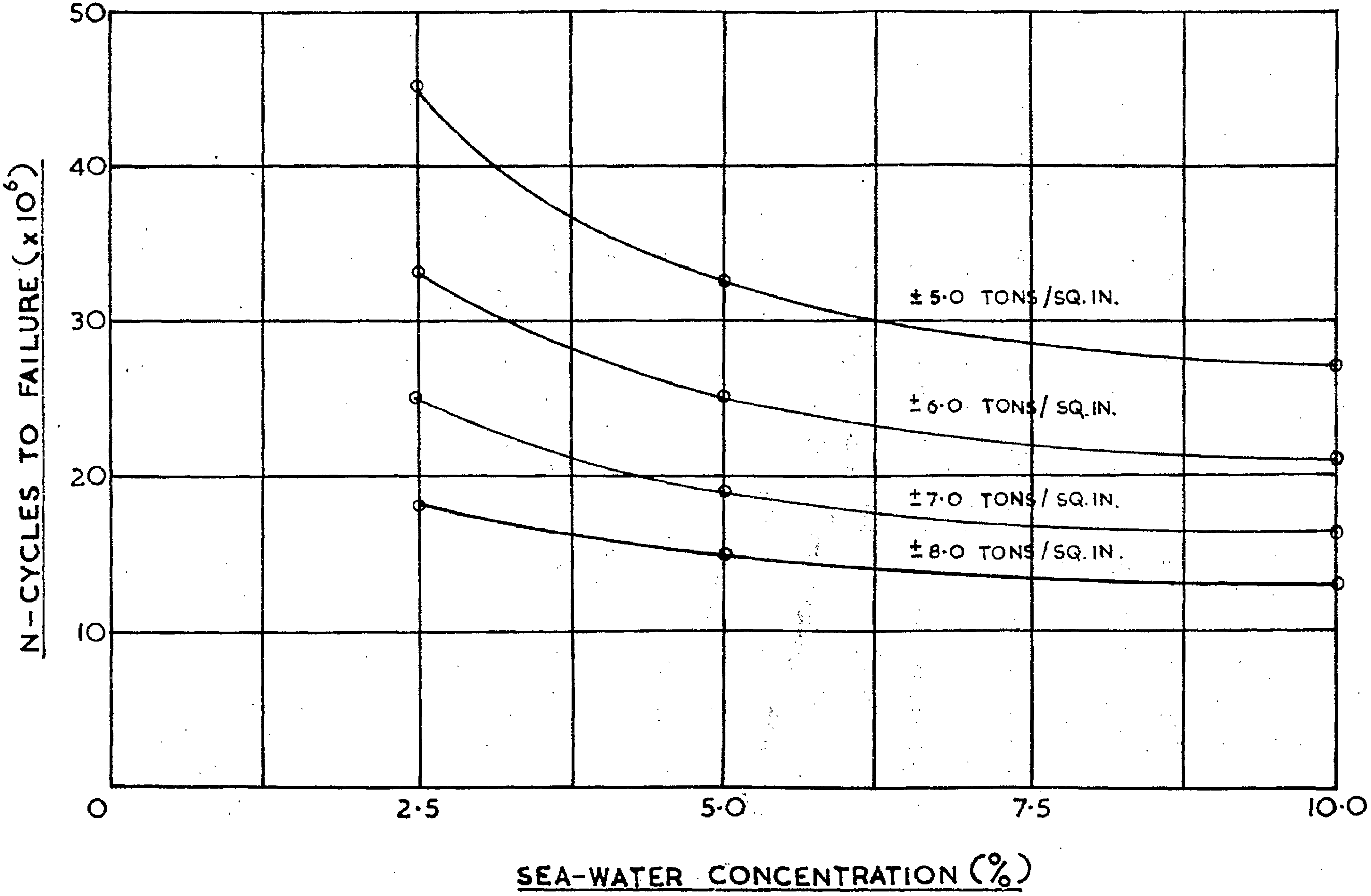
It is suggested by the author that this limiting factor comes into operation at approximately ± 10.7 tons/sq.in. for the material and conditions examined and that this is the cause of the sudden change of the slope at this stress shown by the S-Log N curves presented in Fig.14. This implies a limiting effective stress-concentration factor for a corrosion fatigue crack in mild steel of 1.35.

It is interesting to compare this value with that derived by McAdam(19) from two-stage tests which he carried out on a 0.24 percent carbon steel in the annealed condition. After first subjecting specimens to corrosion fatigue for 20 x 10^6 cycles at 1450 c.p.m. in a natural carbonate water, the subsequent fatigue limit in air of these specimens was determined. The ratio of the fatigue limit in air of the uncorroded material to the fatigue limit in air of the specimens previously subjected to corrosion fatigue (i.e., the effective stress-concentration factor of a corrosion fatigue crack)was found to vary between 1.3 and 1.4, according to the stress employed in the first corrosion fatigue stage.

The effective stress concentration factor for a simple fatigue crack in mild steel has been derived by Frost and Phillips(60). They investigated the stress-endurance characteristics of specimens which had first been partially cracked by simple fatigue in air at stresses above the normal fatigue limit. For these cracked specimens, a stress-endurance curve was obtained showing a distinct fatigue limit at 31 percent of the normal fatigue limit of the uncracked material. Thus, an effective stress-concentration factor of 3.2 may be assumed for a simple fatigue crack in mild steel.

The difference in effective stress-concentration factors for a simple fatigue crack and a corrosion fatigue crack is probably due to geometrical considerations. It is well established that the stress-concentration associated with a notch is an inverse function of the radius at the root of the notch, and it is reasonable to suppose that

FIG. 16. CORROSION FATIGUE LIFE AT CONSTANT STRESS AS A FUNCTION OF SEA-WATER CONCENTRATION

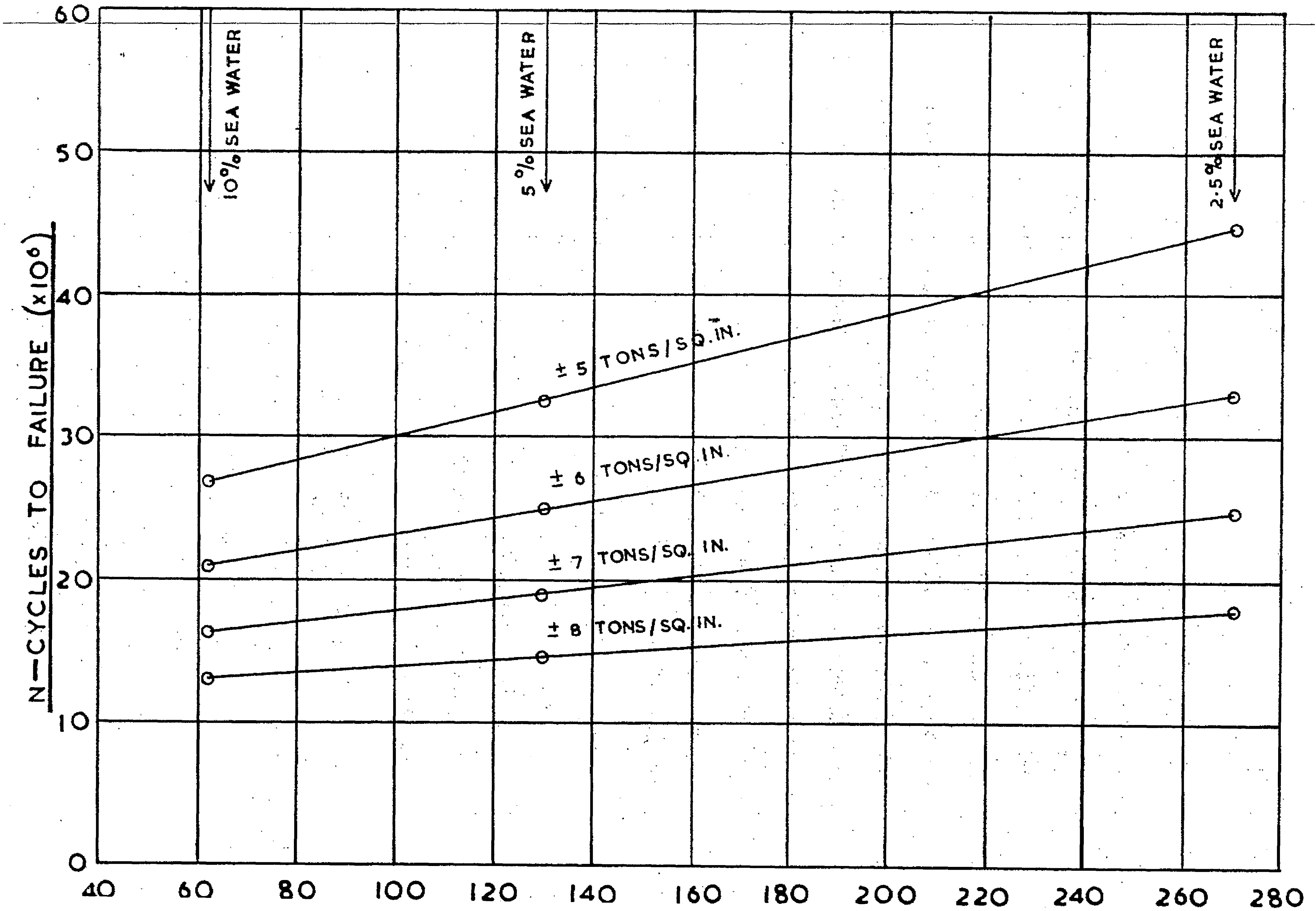


the lower effective stress-concentration factor associated with a corrosion fatigue crack is due to a larger root radius. This explanation is supported by the metallographic appearance of the two types of crack which were contrasted in Chapter 10 (cf. Plates 8 and 9).

It has been shown in the foregoing discussion that the sudden change of slope in the S-Log N curves presented in Fig.14 for the three concentrations of sea-water studied can be accounted for by assuming a limiting value of 1.35 for the effective stress-concentration factor associated with a corrosion fatigue crack in the material tested. A further significant feature of these curves is that the angle of divergence between them increases markedly below the point where the sudden change of slope occurs. This, in effect, means that specimen endurance is much more dependent upon solution concentration at the lower stresses, where simple fatigue does not contribute to failure, than at the higher stresses, where stress-concentration effects are the dominant factor. This observation has led the author to consider further the influence of solution concentration at these lower stresses.

Fig.16 shows the relation between specimen endurance and solution concentration for various levels of cyclic stress. These values have been derived from the S-Log N curves presented in Fig.14, by plotting the intercepts of the curves with lines of constant stress.

FIG.17. CORROSION FATIGUE LIFE AT CONSTANT STRESS AS A FUNCTION OF SOLUTION RESISTIVITY



In view of the suggestion by Evans and Simnad(27) that the increase in electrical resistance between the top and bottom of a corrosion fagitue crack which accompanied the increase in depth of the crack could markedly reduce its rate of propagation, it seemed to the author that the change of solution conductivity with solution concentration might offer an explanation of Fig.16. Accordingly, the specific conductivities of the three solution concentration studied were estimated from data published in International Critical Tables(61). These calculations are detailed in Appendix 1. A graph relating specimens endurance at particular levels of cyclic stress to the specific resistivity of the solutions used is presented in Fig.17. It may be seen that a remarkably linear correlation has been obtained between these two variables. This may be explained by the following concept.

If we consider a corrosion fatigue crack in process of development to be a small electrolytic cell, then the current flowing in that cell will be related to the component parts of the circuit as under.

$$I = \frac{Er}{Ra + Rc + Rm + Re}$$

where I = current flowing in the cell (amps)

Er = reversible electromotive force of the cell (volts)

Ra = resistance due to anodic polarisation (ohms)

Rc = resistance due to cathodic polarisation (ohms)

Rm = resistance of metal between anode and cathode (ohms)

Re = resistance of electrolyte between anode and cathode (ohms)

Thus,

$$Re = \frac{Er}{I} - (Ra + Rc + Rm)$$

Now, if we assume that Er and Ra are functions only of the level of cyclic stress applied to a specimen, and that Rc and Rm are independent of both stress and solution concentration then, at any particular level of cyclic stress;

$$Re \propto \frac{1}{I}$$

since Er, Ra, and Rc and Rm will remain constant.

By Faraday's Law of Electrolysis, the amount of metal removed from the anode is proportional to the quantity of electricity, measured in coulombs, which has been generated.

Thus,

$$Q \propto It$$

where, Q = weight of metal removed from the anode (gms)

I = current flowing in the cell (amps)

t = time for which current flows (secs)

Now, if it is assumed that at a particular level of cyclic stress the endurance of a corrosion fatigue speciemn expressed in cycles (N) is dependent upon the time required to remove a certain weight of metal from the anode of the most critically sited corrosion fatigue crack then,

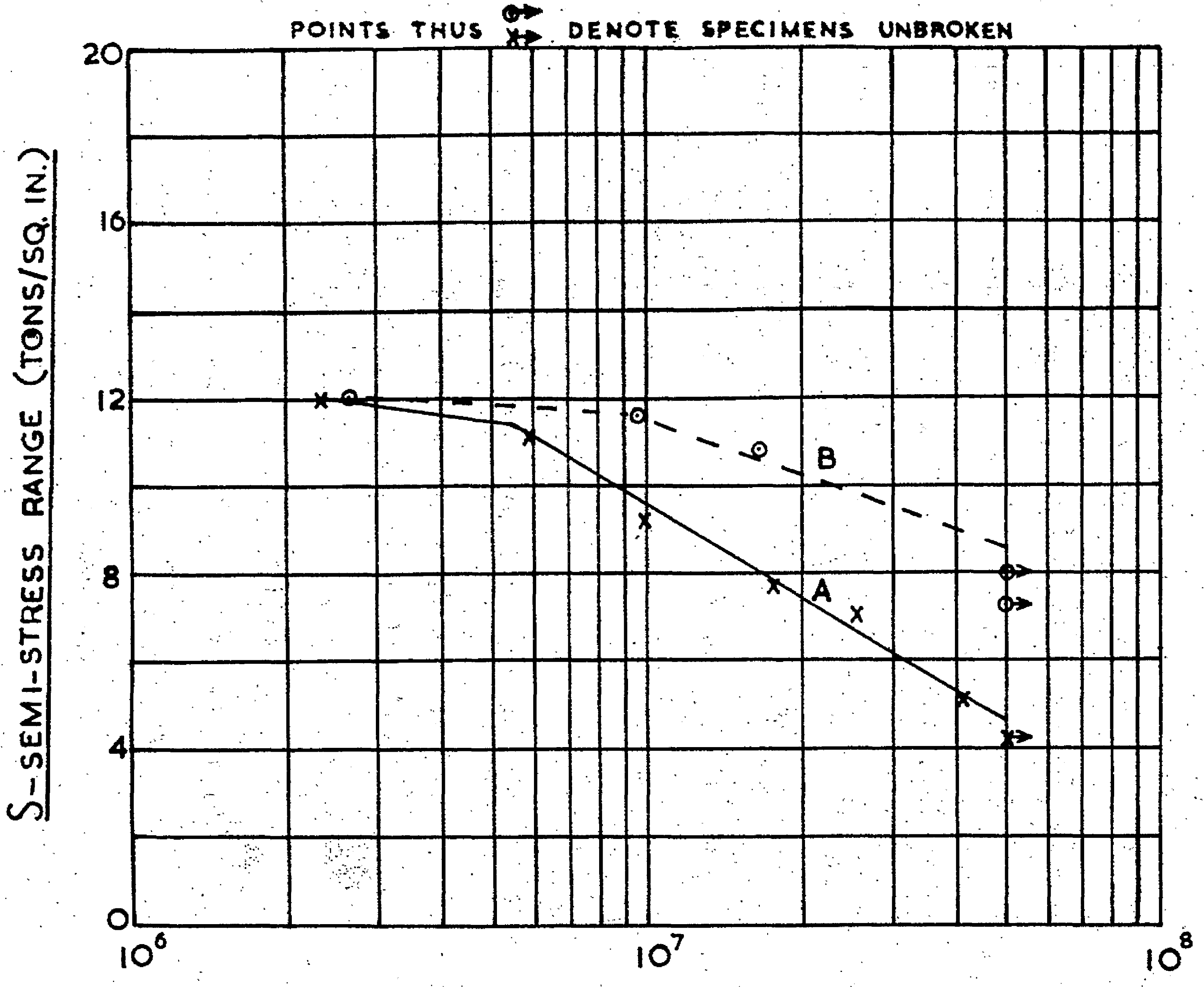
$$N \propto t \propto \frac{Q}{I} \propto Q\ Re$$

Thus a graph of specimen endurance N, at a given cyclic stress against Re, the specific resistivity of the test solution, would be expected to yield a straight line of positive slope. Fig.17 has illustrated that such a linear relationship does exist between N and Re where the level of cyclic stress is constant and the solution varies only in concentration of solute, the chemical nature of the solute being unchanged.

A corollary to this striking dependence of specimen life upon solution conductivity is that for the electrolytic current I to be so dependent upon the factor Re, the average cross-section of the electrolytic path between anode and cathode must be very small. The physical picture which best represents the observed factos is that a corrosion fatigue crack containing electrolyte behaves very much in the same way as a thin metallic strip, providing a considerable electrical resistance between the anode at the crack front and the cathodic areas on the external surface of the specimen. As a crack progresses inwards through the specimen the resistance of the electrolytic path increases and since there is no corresponding increase in the overall electromotive force of the cell, it follows that the intensity of the current I must decrease. Thus, the rate of propagation of a corrosion fatigue crack must decrease with increasing penetration.

This hypothesis explains why so many different corrosion fatigue cracks, in various stages of development, can be found in the one

FIG. 18. S-LOGN CURVES FOR 0·2%C STEEL
(A) IN 2·5% SEA-WATER AT 88°C
(B) IN 2 5% SEA-WATER + 0·05% $K_2Cr_2O_7$ AT 88°C



specimen. In Plates 5 and 6 (Chapter 10), the divergence of the lesser cracks from the principal crack can be interpreted as evidence that these lesser cracks did not start to propagate from the crevice roots until the principal crack had first penetrated sufficiently to alter the stress pattern in the surrounding area. If this principal crack had been continuously accelerating with increasing depth, or even propagating with constant velocity, then it is unlikely that sufficient time would have been available for the lesser cracks to develop to the extent that they obviously have done. Their appearance is consistent with the hypothesis that the principal crack has propagated more and more slowly with increasing depth, so that these lesser cracks, although late in starting, have had sufficient time to develop to the extent shown.

The Effect of Inhibitors on Corrosion Fatigue.

The experimental results obtained from the preliminary survey of the influence of 0.05 percent potassium dichromate upon the corrosion fatigue life of specimens immersed in 2.5 per cent sea-water at 80°C were intended solely as a guide to the selection of a suitable stress level for subsequent experiments. Although only five results were obtained under these conditions, it is of interest to compare the S-Log N curve given by them with the curve for uninhibited 2.5 percent sea-water and the two curves are presented in Fig.18.

The inhibiting influence of 0.05 percent potassium dichromate may be adjudged by comparison of curves A and B in Fig.18. It may be seen that even this small addition of inhibitor has raised the

FIG. 19. INFLUENCE OF INHIBITOR CONCENTRATION ON SPECIMEN ENDURANCE IN 2·5% SEA-WATER AT 88°C.

POINTS THUS x→ Δ→ DENOTE SPECIMENS UNBROKEN

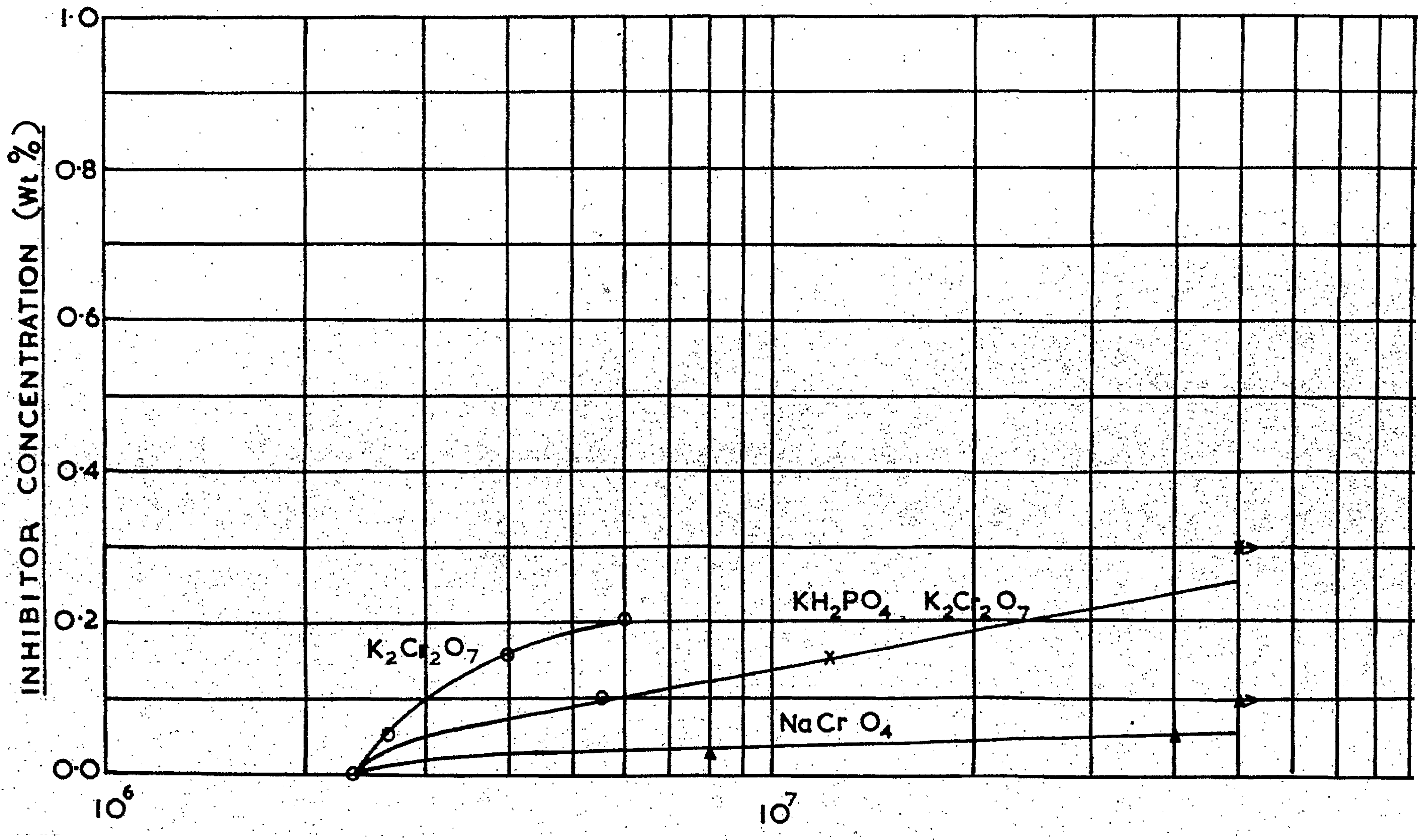
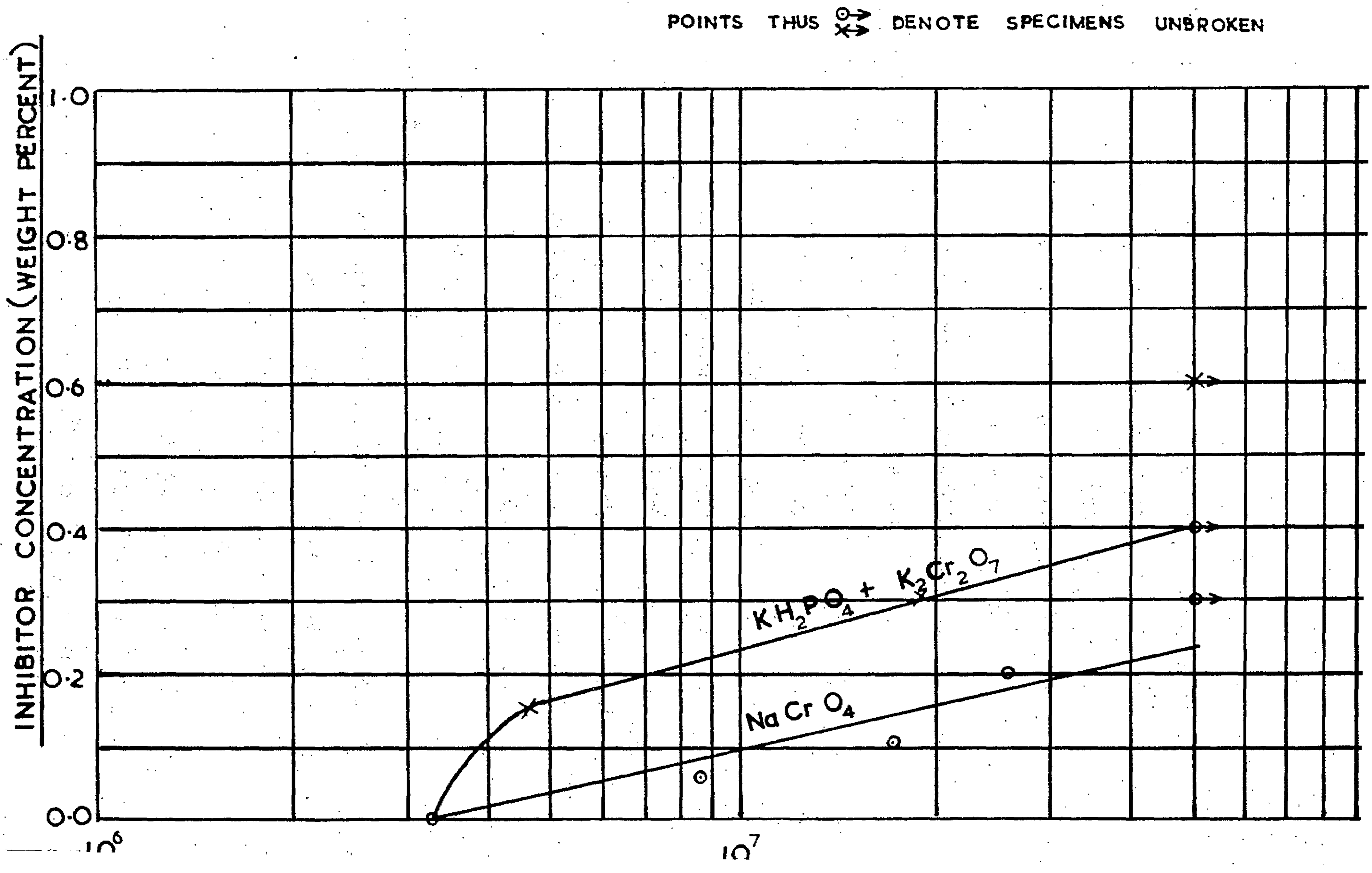


FIG 20 INFLUENCE OF INHIBITOR CONCENTRATION ON SPECIMEN ENDURANCE IN 5% SEA WATER AT 88°C



endurance limit at 50×10^6 cycles in 2.5 percent sea-water from 4.7 tons/sq.in. to approximately 9.0 tons/sq.in. Of particular interest is the convergence of curves A and B at a stress level of 12.0 tons/sq.in. The benefits of small additions of inhibitor, in terms of increased specimen endurance, are therefore much more pronounced at lower stresses than at high.

The divergence of curves A and B at lower stresses is similar to the effect noted previously in Fig.14 where the stress-endurance characteristics in various sea-water concentrations were compared. This analagous behaviour suggests that the addition of potassium dichromate is, in some ways equivalent to the use of a more dilute sea-water environment, and that the inhibitive action persists throughout all stages of the development of corrosion fatigue cracks. Were the inhibitor only active during the initial pitting stage, then curve B could be expected to be above, but approximately parallel to, curve A.

The practical importance of this point is that it holds out promise that the addition of inhibitors to a cooling system where pitting has already occurred would be effective, in some measure, in slowing down the development of corrosion fatigue cracks and so prolonging the working life of the components.

The experimental results contained in Tables 8, 9 and 10 (Chapter 10) are presented graphically in Figs.19 and 20 which illustrate the effect of inhibitor concentration upon the endurance of 0.21 percent Carbon steel at ± 12.0 tons/sq.in. in 2.5 and 5.0

Potassium Dichromate (%)	0.0	0.05	0.10	0.15	0.20
Cycles to Failure(x 10^6)	2.33	2.63	5.49	3.96	5.91

PLATE 13. EFFECT OF INHIBITOR CONCENTRATION ON SURFACE APPEARANCE

(IN 2.5% SEA-WATER AT ±12.0 tons/sq.in.)

percent sea-water. While there can be no absolute basis for the evaluation of inhibitor efficiencies, it is evident, that on the basis of weight percent required to produce a specimen endurance of 50 x 10^6 cycles at ± 12.0 tons/sq.in., sodium chromate is the most effective of the three inhibitors tested. It should be noted, however, that a twofold increase in sea-water concentration requires a fourfold increase in sodium chromate addition to maintain a specimen endurance of 50 x 10^6 cycles. In the case of the phosphate-chromate mixed inhibitor, only about twice as much inhibitor is required to compensate for change from 2.5 to 5.0 percent sea-water.

None of the specimens which were subjected to the action of inhibited sea-water showed complete freedom from corrosive attack. The surface appearance of specimens after tests at ±12.0 tons/sq.in. in 2.5 percent sea-water containing various amounts of potassium dichromate are illustrated in Plate 13.

The most striking feature in the appearance of these specimens is the extreme localisation of attack caused by the inhibitor. This localisation is typical of an inhibitor classified by Evans(34) as "dangerous" in that it increases the intensity of attack although diminishing the overall corrosion rate. It should be noted, however, that despite this localisation, no case was found by the author in which the specimen life was reduced by the addition of a "dangerous" inhibitor.

Potassium Dichromate (%)	0.05	0.10	0.15
Cycles to Failure(x 10^6)	Unbroken at 50.0	Unbroken at 50.0	Unbroken at 50.0

PLATE 14. EFFECT OF INHIBITOR CONCENTRATION ON SURFACE APPEARANCE

(IN 2.5% SEA-WATER AT ±8.0 tons/sq.in.)

Another feature of Plate 13 is the apparent increase in the number of surface pits with increasing inhibitor concentration. This correlation is more apparent than real, however, inasmuch as increasing inhibitor contents have resulted in greater specimen endurances so that more time has been available for the breakdown of points of secondary weakness on the surface.

The truth of this is confirmed by Plate 14. In this case the specimens have all been exposed for the same length of time (50×10^6 cycles) at ± 8.0 tons/sq.in. and the effect of increasing inhibitor concentration is clearly to reduce the number of points of attack on the specimen surface. The differences in the appearances of the three specimens are striking.

The results discussed above are consistent with the general theory of anodic inhibitors outlined in Chapter V. Thus, by repairing and reinforcing the natural oxide film present initially on the specimen surface, the inhibitor effectively increases the resistance to flow of corrosion currents at the anodic areas. The corrosive attack is therefore restricted to the weakest points in the film which the inhibitor is unable to maintain in the face of the cyclic strain which seeks to disrupt this film. With increasing inhibitor concentration, the number of such weak points is reduced and corrosion fatigue is further localised to the points of maximum cyclic strain. Where the inhibitor is present in sufficient quantity to maintain a completely protective film, then no attack at all occurs. The three specimens shown in Plate 14 demonstrate the validity of this theory.

The effect of increasing sea-water concentration on the efficacy of the inhibitors tested has already been discussed. In terms of inhibitor theory, the highly mobile chloride ion may be regarded as being more easily able to penetrate the weak points in the oxide film than the more ponderous hydroxyl ions, so that the effectiveness of the inhibitor is correspondingly reduced.

A feature of the experimental results obtained which is worthy of careful consideration is the fact that, despite the extreme localisation of attack which has been shown to result with certain inhibitor concentrations, no case is recorded where the uninhibited corrosion fatigue life was shortened by the use of such inhibitor concentrations. It has been repeatedly demonstrated by Evans(34,35) and others that, in stressless corrosion, such localisation is invariably accompanied by an intensification of attack at these local areas. It might, therefore, be expected that, under corrosion fatigue conditions, specimen life would be reduced by such localised attack.

The explanation of this apparent anomaly most probably lies in the fact that, under stressless conditions, the corrosion process is under cathodic control, i.e., the intensity of the corrosion currents is determined by the ratio of cathodic to anodic areas. Thus, a reduction of anodic area by "localisation" inevitably results in an increase in intensity of the corrosion currents at the anodic points.

Under corrosion fatigue conditions, however, as the author has previously postulated, the resistance of the electrolyte path within a developing crack is a significant factor and the local corrosion cells are under anodic control. The intensity of the corrosion currents are thus not influenced by the ratio of cathodic to anodic areas. Localisation of attack will not therefore cause intensification and since the inhibitor will tend to increase the anodic resistance at the fronts of developing cracks, an increase in specimen endurance can be expected.

CHAPTER XII.

CONCLUSIONS ON THE NATURE AND MECHANISM OF CORROSION FATIGUE.

A number of conclusions on the nature and mechanism of the corrosion fatigue of mild steel in dilute sea-water may be drawn from the experimental work described and discussed in the previous chapters. These may be enumerated as follows:

(1) There is no limiting value of stress below which corrosion fatigue attack ceases to operate. Failure in dilute sea-water at a value of cyclic stress as low as 20 percent of the fatigue limit in air of the material has been demonstrated. The slope of the S-Log N curves at endurances of 50×10^6 cycles indicates no tendency for these to reach a limiting value.

(2) The path followed by a corrosion fatigue crack in mild steel is transcrystalline and the general direction is perpendicular to the lines of stress in the locality of the crack. The minor deviations in direction from grain to grain are consistent with Gough and Sopwith's(26) hypothesis that the crack follows the traces of the operative slipplanes.

(3) A limiting value of 1.35 may be deduced for the effective stress-concentration factor associated with a corrosion fatigue crack in mild steel. To this limiting factor may be ascribed the sudden change of slope evident in the S-Log N curves derived from tests in dilute sea-water.

(4) Where stress-concentration at the root of a corrosion fatigue crack is sufficient to raise the nominal stress above the true fatigue limit in air of the material, failure results from the rapid propagation of a simple fatigue crack.

(5) At low values of nominal stress where the true fatigue limit of the material is not exceeded even at points of maximum stress concentration, failure results from the slow propagation of a corrosion fatigue crack.

(6) The effect of increasing the solution concentration within the range 0 to 10.0 percent sea-water is to reduce the specimen endurance for any particular value of cyclic stress.

(7) The decrease in specimen endurance caused by increasing sea-water concentration is not particularly severe at values of cyclic stresses where failure results from simple fatigue crack propagation. The effect may be ascribed to the more rapid development of the surface pits from which final failure is initiated.

(8) At low values of nominal stress where failure results from the slow propagation of corrosion fatigue cracks, the influence of sea-water concentration is pronounced. There exists a linear correlation between specimen endurance at low stresses and the specific resistivity of the corrosive media which may be predicted from the electrochemical theory of corrosion.

(9) A controlling factor in the rate of development of a corrosion fatigue crack is the resistance of the electrolyte path contained in the crack. A necessary consequence of the increase in the resistance of this path with increasing penetration is that the propagation of a corrosion fatigue crack proceeds at a diminishing rate.

(10) The addition of potassium dichromate, sodium chromate or a mixture of potassium dichromate and potassium di-hydrogen phosphate to dilute sea-water markedly decreases the severity of corrosion fatigue attack on mild steel. On a basis of weight percent, sodium chromate is the most effective of these inhibitors.

(11) The effect of increasing inhibitor concentration, within the ranges studied, is to reduce the number of points of attack on the specimen surface and to reduce the rate of propagation of corrosion fatigue cracks from these points.

(12) The extreme localisation of attack, characteristic of the three anodic inhibitors tested, does not necessarily result in a reduction in the specimen life at a given value of cyclic stress. This may be interpreted as an indication that the rate of corrosion fatigue crack propagation is under anodic control.

FIG. 1A. EQUIVALENT CONDUCTIVITY OF NaCl aq AT VARIOUS TEMPERATURES AS A FUNCTION OF CONCENTRATION

(DATA FROM INTERNATIONAL CRITICAL TABLES (61))

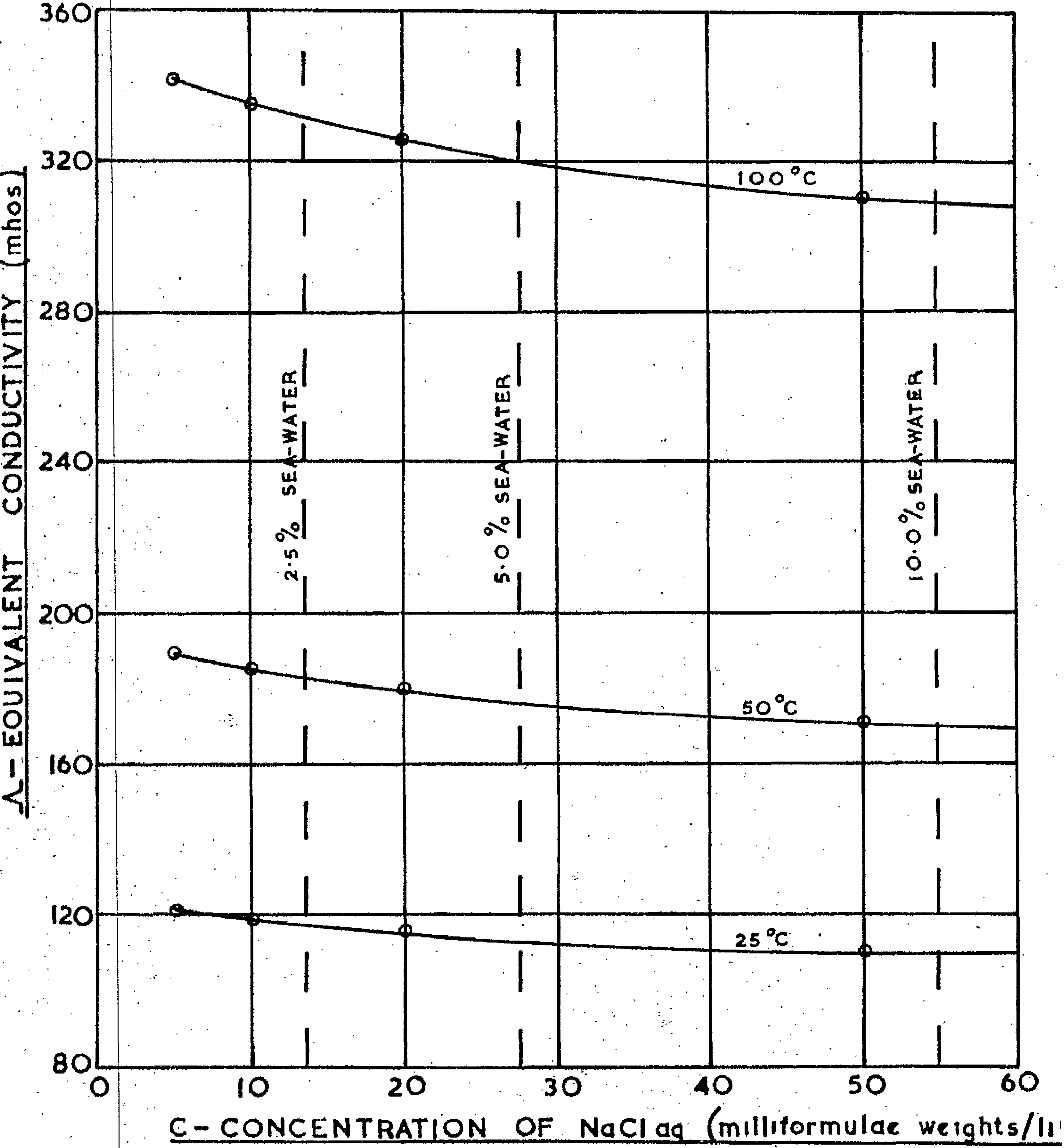
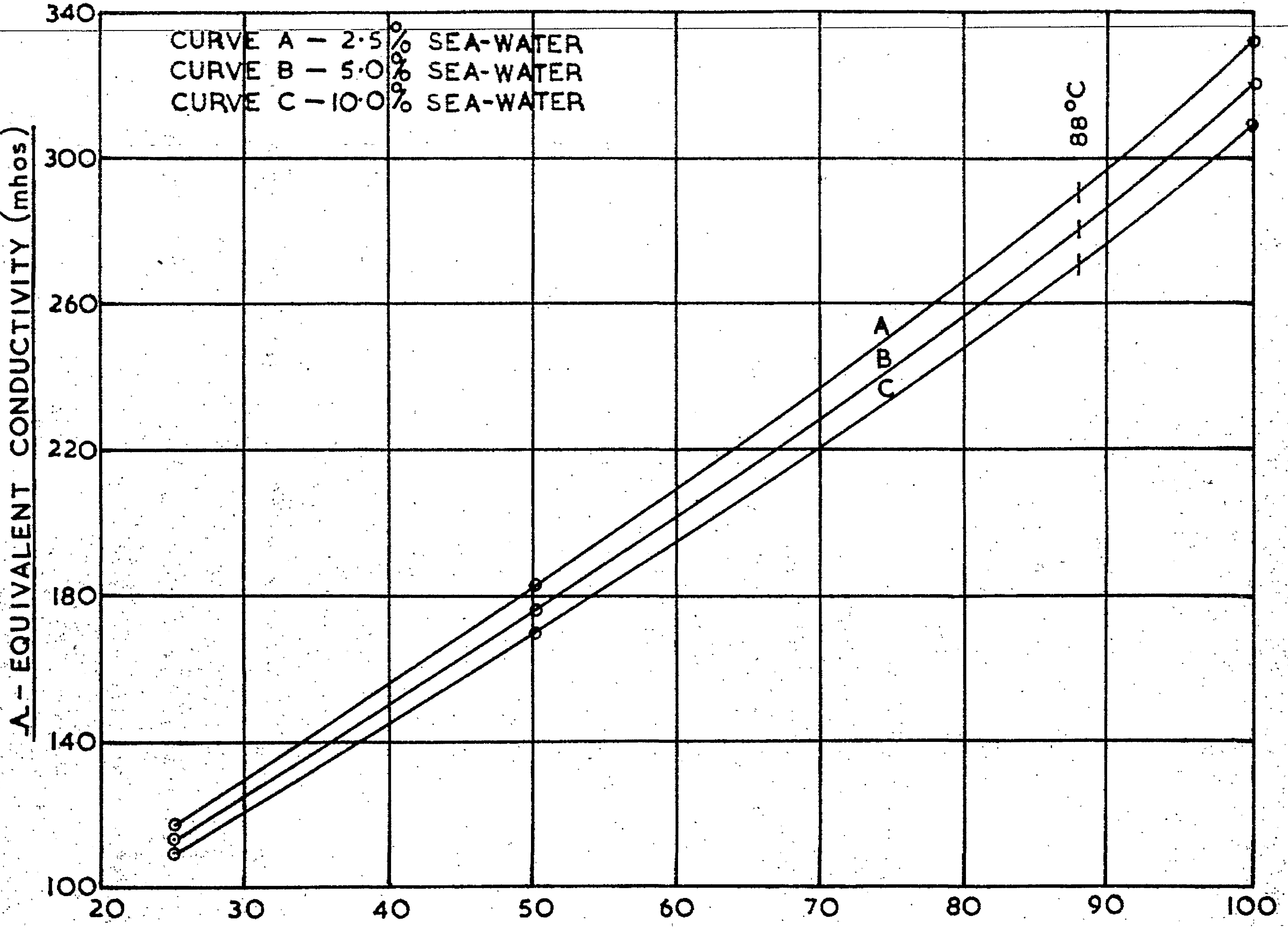


FIG. IB. EQUIVALENT CONDUCTIVITY OF NaCl aq. AT VARIOUS CONCENTRATIONS AS A FUNCTION OF TEMPERATURE



APPENDIX.

Calculation of Conductivity of Dilute Sea-Water at 88°C.

No experimental determination of the electrical conductivity of dilute sea-water at temperatures around 88°C would appear to have been published. Such figures are, however, available for sodium chloride solutions of various concentrations and an estimate can be made of sea-water conductivities by calculation of the conductivities of sodium chloride solutions of equivalent chloride content.

Values of the equivalent conductivity (Λ) of dilute sodium chloride solutions, as published in the International Critical Tables(61), are shown in Figure 1A for 25°C, 50°C and 100°C. Allowing for the presence of NaCl, KCl and $MgCl_2$ in the synthetic sea-water used in the corrosion fatigue experiments, and neglecting the influence of the small amounts of $NaHCO_3$, KBr, $CaSO_4$ and $MgSO_4$ involved (cf. Table 3, page 49), the equivalent concentration of NaCl in 100% sea-water is 32.1 gm/litre. Thus, the equivalent concentrations of 2.5%, 5% and 10% sea-water are respectively 13.7, 27.5, and 54.9 milliformulae weights/litre.

Figure 2A shows the values of equivalent conductivity (Λ) obtained from Figure 1A for these three sea-water concentrations plotted against temperature. From these curves, values of Λ at 88°C have been obtained and are presented in Table 1A which also tabulates the values of specific conductivity (K) and specific resistivity (ρ) which may be calculated from the relationship,

$$\rho = \frac{1}{K} = \frac{10^6}{C}$$

where, ρ = specific resistivity (ohms/cm.cube).

K = specific conductivity (mhos/cm.cube).

Λ = equivalent conductivity (mhos).

C = concentration of solute (milliformulae weights/litre).

TABLE 1A.

Electrical Conductivity of Dilute Sea-Water at 88C° (Calculated Values).

Sea-water concentration (%)	Equivalent NaCl concentration (milliformulae weights/litre)	Equivalent Conductivity (Λ) (mhos).	Specific Conductivity (K) (mhos/cm. cube).	Specific Resistivity (ρ) (ohms/cm. cube).
2.5	13.7	270.8	0.00370	270.0
5.0	27.5	280.0	0.00770	130.0
10.0	54.9	290.8	0.01599	62.5

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CORROSION FATIGUE OF MILD STEEL.

by J.M. Cairney.

SUMMARY.

In a survey of published work which forms the first part of this thesis, the author has firstly considered the basis of the electrolytic theory of corrosion as applied to the corrosion of steel in aqueous media. This is followed by an examination of the published researches on corrosion fatigue which have appeared since the pioneer work of Haigh in 1917. The known characteristics of the phenomenon are discussed and a critical analysis of the influence of various factors, material and environmental, is attempted. In a consideration of the various theories which have been advanced to explain corrosion fatigue, emphasis is laid upon the divergencies between these theories. A further chapter dealing with the published work relating to the theory and application of chemical inhibitors draws attention to the lack of experimental data on the use of such inhibitors under corrosion fatigue conditions.

Part II of the thesis describes the experimental aspects of the research conducted by the author on the corrosion fatigue of mild steel in distilled water, in varying concentrations of sea-water, and in sea-water solutions containing inhibitors. The relation of these experimental determinations to service conditions obtaining in water-cooled diesel engine piston rods is examined and the design, construction and operation of apparatus capable of applying fatigue stresses to a specimen immersed in a circulating solution at 38°C is considered in some detail.

The experimental results obtained by the author and some metallographic features of the specimens used are discussed at length in Part III of the thesis. It is suggested that two modes of failure can occur under corrosion fatigue conditions. Where stress-concentrati at the root of a corrosion fatigue crack is sufficient to raise the nominal stress above the true fatigue limit in air of the material, failure results from the rapid propagation of a fatigue crack. At low values of nominal stress, however, where the true fatigue limit of the material is not exceeded even at points of maximum stress-concentration, failure results from the slow propagation of a corrosion fatigue crack. The transition from one mode of failure to the other is shown to be consequent upon a limiting effective stress-concentration factor for mild steel of 1.35, and to give rise to a sudden change of slope in the S-Log N curves derived from tests in dilute sea-water.

The effect of increasing sea-water concentration in reducing specimen life within the range 0 to 10.0 percent, is shown to be most pronounced at low values of nominal stress. A linear correlation which was found to exist between specimen endurance at low stresses and the specific resistivity of the corrosive media, is explained on the basis of the electrochemical theory of corrosion. The influence

of the resistance of the electrolyte path contained within a corrosion fatigue crack upon the rate of propagation of the crack is discussed.

The nature of the inhibiting action of potassium dichromate, sodium chromate, and a potassium dichromate-potassium dihydrogen phosphate mixture upon corrosion fatigue in dilute sea-water is reviewed in the light of inhibitor theory. The absence of intensified attack, despite the marked localisation of pitting which is characteristic of the three anodic inhibitors tested, is interpreted as evidence that the development of a corrosion fatigue crack is under anodic control.