RAPID FRACTURE INDUCED BY CORROSION OF ULTRA-HIGH STRENGTH STEELS UNDER STRESS

by

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ABSTRACT

The failure by cracking of two ultra-high strength steels, Rex.539 and En.40C, under conditions of stress-corrosion has been studied. The steels were heat-treated to strength levels near 120 t.s.i. Application of sodium chloride and other corrodents to notched tensile test-pieces loaded at 33, 50, 70 and 80% of their breaking load resulted in fracture within a few weeks, or even within an hour, except at the lowest stress when life exceeded 8 weeks.

The higher silicon steel, Rex.539, proved the less susceptible (i.e. had longer life). For both steels a wide scatter in stress-corrosion lives seemed to be a feature of the phenomenon studied. The life-range/stress relationship and other characteristics could best be explained by a mechanism based on embrittlement by hydrogen resulting from corrosion, the stress-concentration at the notch promoting its absorption.

The time-to-failure by this mechanism is at least partly controlled by the rate at which hydrogen accumulates by diffusion at the zone of maximum triaxial stress just beneath the notch-root. Thus the mechanism applies strictly to notched test-pieces only.

Similar failures were observed with cadmium-plated specimens which had been de-embrittled by baking. Very thin coatings accelerated cracking by galvanic action, but thicker coatings delayed cracking by protecting the steel from corrosion.
ACKNOWLEDGEMENTS

Grateful acknowledgements are made to Metallic Surfaces Research Laboratories Ltd., in whose premises much of the work was done, and to the Ministry of Aviation for sponsoring the investigation.

Thanks are due to Professor L.W. Derry, Dr. R.L. Samuel and Mr. H.G. Cole for useful discussion and guidance; to Mr. P.R. Weddon (Fairey Aviation Co. Ltd.) for advice on the heat-treatment of En.40C, and for checking the absence of retained austenite; to Dr. K. Bolton (Battersea College of Technology) for determination of the hydrogen content of the steels, and to Dr. B.L. Daniell for kindly reading the draft of this thesis.

Lastly the author wishes to thank his wife for typing both the draft and final versions.
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1. INTRODUCTION

The work which forms the subject of this thesis arose from a project concerned with the hydrogen embrittlement of "ultra-high tensile" steels. These steels, especially when heat-treated to an ultimate tensile strength in excess of 100 tons/sq. in., are very sensitive to embrittlement by hydrogen absorbed during acid pickling, and cathodic processes such as electroplating, and the aim of the original project was to devise protective coating techniques which would avoid the embrittlement commonly associated with electroplating.

This embrittlement shows up in the delayed failure of components in service at stresses well below the ultimate tensile strength of the steel, and the time dependent nature of the phenomenon determines the type of test used for its detection. Normal tensile tests, and other tests involving fairly rapid loading, are not sufficiently sensitive to hydrogen embrittlement and sustained load tests, or tests where the rate of straining is slow, are required. Sustained load tests are generally regarded as most sensitive, notched tensile test-pieces or notched C-rings being often used.

The notched tensile test-pieces and spring-loaded rigs used for the hydrogen embrittlement investigation were described by Samuel and Lockington, who found that when coated test-pieces under load were submitted to accelerated corrosion (3% sodium chloride solution) failure was more rapid, and that uncoated test-pieces also fractured when submitted to corrosion while under stress.
This previous work has been mentioned here to explain the types of test-piece and equipment used in the present work, to explain the approach to the problem and also to explain the title, where the expression "fracture induced by corrosion" is used in preference to "stress-corrosion cracking", to contrast with "fracture induced by hydrogen". However the term "stress-corrosion" is used when describing and discussing the work.

In many stress-corrosion systems, the corrodent is specific and the range of conditions confined within narrow limits, often at the borderline between the active and passive conditions of the metal; times to fail are fairly reproducible. The limits of conditions and composition of corrodent are much wider in the work described here; a stress-concentration, as at the root of a notch, is necessary; times to fail are scattered over a wide range and are only slightly affected by stress level at intermediate stresses. The last two points are in keeping with hydrogen embrittlement observations.

For acid corrodents, there is no doubt that hydrogen is available, but the possibility of producing hydrogen by corrosion of steel in neutral environments, as in the present investigation, is open to argument. The actual quantity of hydrogen (concentrated at the notch) necessary to embrittle is likely to be very small, and its detection would be very difficult; evidence must, therefore, be circumstantial, or indirect.

As the stress-corrosion work followed from hydrogen embrittlement
experiments, and similarities between the two were apparent, a working hypothesis based on a hydrogen embrittlement mechanism was assumed. Sustained load tests were made on notched test-pieces to which several different salt solutions were applied as a spray or as drops. Cadmium-plated test-pieces were included as these steels are commonly protected with cadmium in aircraft and as it was more likely that cathodic hydrogen would be generated on a steel surface coupled with cadmium. The effect of chromate additions to the corrodent was also determined, as an oxidising agent could affect hydrogen availability and absorption.

The hydrogen embrittlement work, various coating experiments, and the greater part of the stress-corrosion test results formed a report to the Ministry of Aviation (1). No attempt was made to define the mechanism of the corrosion induced failure closely; the suggestions made and conclusions reached at that stage have been reproduced at the beginning of the discussion (4.2). The survey of literature in the next chapter has been brought up to date. Since the corrosion induced failure falls within the accepted definition of stress-corrosion cracking, and appears to be an effect of hydrogen embrittlement, the survey covers ideas on the mechanism of both hydrogen embrittlement and stress-corrosion, and also other cracking processes. Unfortunately, this leads to a rather lengthy survey. The recent literature on the stress-corrosion of high strength steels has not generally supported the hydrogen embrittlement mechanism proposed here;
papers have tended to reject the possibility of hydrogen embrittlement except for steels in the fully martensitic condition or for acid environments.

The proposed mechanism has been developed in greater detail in the discussion, and some supporting evidence for this was derived from observations made during the course of the work, but whose importance was not appreciated at the time. The literature on the hydrogen embrittlement of ultra-high strength steels has provided a useful background.

The discrepancy between the conclusions reached here and the opinions expressed by other investigators is probably explained by testing technique and more particularly by the type of test-piece used. The balance between cracking by an "active path" mechanism (stress-corrosion cracking in the narrow sense) and by hydrogen embrittlement is a delicate one, and small differences in detail may determine which mechanism prevails under each set of conditions.

NOTE. A number of ultra-high strength steels are mentioned in the next chapter, and so for convenience, composition specifications are tabulated overleaf.
TABLE I. Compositions of some Ultra-High Strength Steels (%).

<table>
<thead>
<tr>
<th>Specn</th>
<th>En.26</th>
<th>En.40c</th>
<th>Rex.539</th>
<th>AISI/SAE 4330M</th>
<th>AISI/SAE 4340</th>
<th>AMS 6427</th>
<th>AMS 6407</th>
<th>AMS 6410</th>
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<tr>
<td>Ref.</td>
<td>B5. 970 1955</td>
<td>94.220</td>
<td>222</td>
<td>**</td>
<td>110</td>
<td>110</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.36/.44</td>
<td>0.30/.50</td>
<td>0.38</td>
<td>0.33</td>
<td>0.36/.43</td>
<td>0.30</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>Si</td>
<td>0.10/.35</td>
<td>0.10/.35</td>
<td>1.5</td>
<td>0.28</td>
<td>0.20/.35</td>
<td>0.30</td>
<td>0.62</td>
<td>0.40</td>
</tr>
<tr>
<td>Mn</td>
<td>0.50/.70</td>
<td>0.40/.80</td>
<td>1.5</td>
<td>0.89</td>
<td>0.60/.80</td>
<td>0.86</td>
<td>0.74</td>
<td>1.28</td>
</tr>
<tr>
<td>S, P</td>
<td>0.05 max.</td>
<td>0.05 max.</td>
<td>0.02</td>
<td>0.013</td>
<td>0.04 max.</td>
<td>0.04</td>
<td>0.013</td>
<td>0.013</td>
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<tr>
<td>Ni</td>
<td>2.3/2.8</td>
<td>4.0 max.</td>
<td>1.75</td>
<td>1.95</td>
<td>1.65/2.00</td>
<td>1.80</td>
<td>2.08</td>
<td>1.75</td>
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<tr>
<td>Cr</td>
<td>0.6/0.8</td>
<td>2.5/3.5</td>
<td>0.96</td>
<td>0.70/0.90</td>
<td>0.86</td>
<td>1.15</td>
<td>-</td>
<td></td>
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<tr>
<td>Mo</td>
<td>0.4/.7</td>
<td>0.7/1.2</td>
<td>0.4</td>
<td>0.45</td>
<td>0.2/.3</td>
<td>0.45</td>
<td>0.44</td>
<td>0.36</td>
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<tr>
<td>V</td>
<td>0.1/.3</td>
<td>0.2</td>
<td>0.09</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Cu</td>
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<td>0.21</td>
<td>0.17</td>
<td>0.14</td>
<td>-</td>
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* Typical composition

** Usual specification. A high silicon modification has been introduced, 300M, 1.75% Si (231).
2. CORROSION, HYDROGEN EMBRITTLEMENT and STRESS-CORROSION -- A SURVEY OF THE LITERATURE.

2.1. Introductory Note  The effect studied in the present work can clearly be classified under the broad heading of "stress-corrosion cracking", and this must form the central topic of this survey. The literature on stress corrosion cracking is quite extensive, but often relates to specific systems which have attracted attention. The published work in the more limited field of the stress-corrosion of high-tensile steels (or, indeed steels in general) in saline solutions has been comparatively recent. However, the related topic - the delayed failure of high-strength steels under stress attributed to hydrogen absorption from various sources has been studied in detail and there is an extensive literature in the form of papers and reports.

This survey refers first to three topics, corrosion of steel, hydrogen in steel, and crack propagation, in order to bring out certain points useful in interpreting the results of the present work and also to form a basis for the discussion of the literature on delayed failure by hydrogen embrittlement, and on stress-corrosion cracking. This last topic will be considered in a general way, and then more particularly as related to high-strength steels and the possible connections with hydrogen embrittlement.

2.2. Corrosion of Steel

2.2.1. General Corrosion Reactions  It is assumed that the principles
of electrochemistry, as relating to corrosion, are well understood, and
that it is unnecessary here to define the terms used. The subject is
well covered in a number of standard works, for example by Evans (2,3),
Uhlig (4,5) and Shroir (6), as well as in numerous papers (e.g. (7,8,9,15)).

When iron corrodes in salt solutions, of the two main possible
anodic reactions, the oxidation of iron to ferrous ions fits the observed
behaviour better (9). The reaction is usually written:

\[
Fe \rightarrow Fe^{+++} \text{aq.} + 2e
\]

The precipitation of ferrous corrosion products follows at a distance
from the metal surface depending on the conditions; further oxidation
to ferric products may occur in the presence of dissolved oxygen, or
oxidising agents. The second possibility, the direct formation of
an oxide or other film at the metal surface is only likely in the
presence of inhibiting ions (section 2,2,2) or with applied anodic
potential. Such a reaction may be written:

\[
2Fe + 6 OH^- \rightarrow Fe_2O_3 + 3H_2O + 6e
\]

The cathodic reaction, in the absence of dissolved oxygen or
reducible ions, is the reduction of hydrogen ions to form first an
adsorbed film and then bubbles of the gas:

\[
2H^+ + 2e \rightarrow 2H \rightarrow H_2
\]

Dissolved oxygen provides a second cathodic reaction:

\[
\frac{1}{2}O_2 + 2e + H_2O \rightarrow 2 OH^-
\]

Other cathodic reactions may be the reduction of ions such as Fe^{+++},
\[CrO_4^{2-}, \text{ and NO}_2^-,\] or of oxide films (10), which is reaction 2 in
reverse.
21.

The standard electrode potential for reaction 1 is -0.44 volts\(^{(11)}\). (All potentials quoted are measured against a normal hydrogen electrode, using the European sign convention). For iron in salt solutions, the equilibrium potential for the reaction is near -0.6 volts, assuming a concentration of Fe\(^{++}\) of \(10^{-6}\) g ion/litre (as in Pourbaix's simplified diagrams\(^{(12-14)}\)).

For cathodic reaction 3, the equilibrium potential in neutral solutions is -0.414 volts, so iron should just corrode with the evolution of hydrogen\(^{(15)}\); at potentials between -0.6 and -0.414, both reactions 1 and 3 should proceed\(^{(14)}\). However, taking polarisation into account, it is generally considered unlikely that the anodic reaction could produce and maintain a sufficiently low potential to provide the overpotential for hydrogen evolution (see, for example, ref. 16 p. 333\(^{t}\)). A potential of -0.364 volts has been quoted for steel in aerated moving sea-water (ref. 6, p. 2.31).

It is a fact that iron does not corrode to any extent in de-aerated neutral solutions. The cathodic areas are quickly polarised by a film of adsorbed hydrogen, and corrosion can only proceed if this hydrogen is removed as a gas or chemically by a "cathodic depolariser" such as dissolved oxygen\(^{(17)}\). Hence in aerated neutral solutions, the resultant cathodic reaction is oxygen reduction, and the corrosion rate is controlled by the availability of dissolved oxygen. Other oxidising agents will depolarise the cathodes, and even soil bacteria can have this effect\(^{(18)}\).
The action of oxygen is not accepted by all authorities as "depolarising the cathodes"; direct cathodic reduction of oxygen may be preferred—see, for example, Evans' footnote, ref. 3, p. 275.

However, it was found by Bengough and Lee (19), and confirmed by Evans and Hoar (8), that hydrogen was slowly evolved when mild steel corroded at 25°C, totally immersed in 0.5N sodium or potassium chloride solutions aerated with air or oxygen. Using oxygen, and measuring the volumes of oxygen absorbed and hydrogen evolved, they found that the hydrogen evolved corresponded to about 5% and the oxygen absorbed to the remainder of the total corrosion. In natural sea-water, the amount of hydrogen evolved was often equivalent to about half the total corrosion; this high figure was attributed to the presence of organic material in the sea-water. In the absence of oxygen, there was no hydrogen evolution.

2.2.2. Passivity and Pitting Corrosion When a metal, although thermodynamically unstable in an environment, does not corrode or only corrodes slowly, it is said to be passive. Passivity is generally associated with the direct formation of an oxide or other film by anodic reaction, giving protection to the anodic areas, or in a wider sense by precipitation of sparingly soluble corrosion products on to the metal surface. Passivity of iron in water, as indicated by the Pourbaix diagram (12-14) is expected at a pH above 8.5, when the anodic reaction tends to produce films of magnetite, or at a higher potential, ferric oxide. At pH 7, and above -0.2 volts, ferric oxide can be formed.
by oxidation of ferrous ions at the anodes.

Oxidising agents can also promote the formation of a film, especially in the presence of dissolved oxygen, a potential rise into the passive range ensuing. The film-forming ability of other anions is referred to later.

The presence of a film of $\gamma$-Fe$_2$O$_3$ on passive iron has been demonstrated, but Uhlig has maintained that it is strong adsorption of passivating ions, thus reducing surface activity, that is responsible for passivation. In this connection, Young has pointed out that the Flade potential does not coincide with any reversible oxide potential. Tomashov and other Russian authors take the view that the two processes are complementary, adsorption preceding film formation.

Pitting, the normal mode of corrosion of steel in aerated neutral saline solutions, may be regarded as a breakdown of passivity. Pit sites may be pores or cracks in the air-formed film, defects or inhomogeneities in the steel, or may originate from statistical fluctuations in conditions or from local cold work. A cell is formed, which may be represented as:

$$\text{O}_2 \text{ on oxide surface / electrolyte / metal at base of pore}$$

The stages by which the pore is converted into a pit have been described by Hoar. Conditions develop which perpetuate the pit and pit growth rate may even increase with time.
Factors contributing to continued growth of a pit include the reduction of pH and depletion of film repairing ions within the pit, the diffusion of chloride ions into the pit to balance the ferrous ions produced there, and the differential aeration effect between the pit and the large filmed cathodic area.

Chloride and chlorate ions tend to cause film breakdown and thus promote pitting. Sulphate ions promote pitting to a lesser extent. Film-repairing ions — anodic inhibitors, passivators — include OH\(^-\), CO\(_3\)^-, NO\(_2\)^-, CrO\(_4\)^-, PO\(_4\)^-, SiO\(_3\)^-, acetate and benzoate. When these are in sufficient concentration within a pore, the corrosion product tends to be insoluble and so plug the pore. Ferric products are less soluble than ferrous products, so oxidising anions are more effective, especially if the pH in the pore falls below 5. Pryor and Cohen showed that non-oxidising anions required dissolved oxygen to be fully inhibitive, and even with chromate and nitrite there was evidence that the passivating film of \(\alpha\)-Fe\(_2\)O\(_3\) was mainly formed by dissolved oxygen if present.

Passivation by anodic inhibition, particularly with oxidising anions, is often "dangerous" in the sense used by Evans, since such ions act as cathodic depolarisers and thus intensify corrosion unless their concentration is sufficient to passivate the anodes fully. Cartledge has shown that chromate ions can supply at least part of the cathodic current. The cathodic activity of chromate ions was also demonstrated by Powers and Hackerman, using \(^{51}\)Cr as a tracer; when steel corroded actively in dilute (10\(^{-4}\)M) chromate...
solution, the cathodic areas and loose corrosion products were radioactive.

How chromate ions passivate the anodic areas is not fully understood. Film stripping experiments (32) and tracer techniques (31) have shown little chromium in the oxide film. Dissolved oxygen is necessary for full effectiveness (24, 29), but direct or indirect oxidation by chromate ions to form ultimately $\gamma$-$\text{Fe}_2\text{O}_3$ is often assumed (20, 26). Chromate adsorption has been proposed (21), and Pourbaix (12) considered that conditions where $\text{Cr(OH)}_3$ was the stable species, rather than $\text{Cr}^{++}$ or $\text{Cr}^{+++}$, produced passivity. Stern (33) proposed that the oxidising inhibitor increases the cathodic reaction rate, and hence the intensity of the anodic reaction to such an extent that the potential rises into the passive range. Thus it is unnecessary to assume any anodic action by the chromate.

Hoar and Evans (32) described the changes in corrosion pattern as chromate is added to chloride solutions. Very little chloride is necessary to break down passivity in chromate solutions - about 1300 p.p.m. potassium chloride in 0.1 N chromate (29). Matsuda and Uhlig (34) derived an expression from experimental results giving the critical concentration of chloride or sulphate to cause pitting in chromate and nitrite solutions. If $M_p$ and $M_s$ are the molar concentrations of passivator and added salt respectively, then $\log M_s = a + b \log M_p$.

For $\text{NaCl/Na}_2\text{CrO}_4$ mixtures, $a = -1.19$ and $b = 0.85$. 
2.2.3. **Intergranular Corrosion**  The conditions for intergranular corrosion, i.e. selective attack at grain boundaries, have been briefly discussed by Evans\(^{(25)}\). Localised attack may be at anodic grain boundary precipitates, or the disordered lattice at high angle boundaries may be anodic, particularly under critical conditions (e.g. near the active/passive potential for the alloy).

Attacks may be further concentrated at suitably oriented boundaries by an applied stress\(^{(25)}\), so that there is a connection with stress-corrosion. At a later stage, the mechanisms of pitting corrosion and crevice corrosion may apply.

2.2.4. **Crevice or Contact Corrosion**  Corrosion in crevices, i.e. where a metal surface is closely shielded by near contact with another body, or where the metal itself is cracked, has importance in stress-corrosion cracking. The conditions in a crevice resemble conditions in a growing pit, so similar factors are applicable. Differential aeration\(^{(35)}\) is an important factor, but as Rosenfeld and Marshakov\(^{(36)}\) point out in discussing the mechanisms, crevice corrosion also occurs in acid electrolytes in the absence of oxygen. Metals in the passive state, near the Flade potential, or in the presence of critical concentrations of passivating anions, are especially sensitive to crevice corrosion\(^{(36)}\).

2.2.5. **Effect of Strain on Corrosion**  The information on this subject was discussed by Harwood in 1950\(^{(37)}\), and more recently at least two authors have summarised the position in presenting their own work\(^{(38, 39)}\). The reported effects are confused\(^{(37)}\) because
the two cathodic reactions (hydrogen evolution, oxygen absorption) have not always been distinguished, and because it is difficult to separate the effects of stress/strain on the oxide film and on the metal beneath.

Stress in the elastic range is not expected to have a measurable effect, except in altering the state of repair of oxide films, as was suggested by Evans and Simnad; however Nobe and Tan did show small (approx 1 mV) potential changes in the anodic direction on both loading and unloading. Plastic strain (cold-worked materials have often been compared with annealed materials) has been generally found to increase corrosion rates in acids. In neutral solutions no such effect is observed, the explanation being that the corrosion rate is controlled by availability of dissolved oxygen. Skapski and Chyzenski concluded that no increase in corrosion rate occurred when the pH was greater than 4, except in sodium chloride solution containing hydrogen peroxide, where presumably availability of oxygen was not a rate controlling factor.

The increase in corrosion rate is partly accounted for by stored plastic strain energy, which could lower the electrode potential by a few millivolts, localised sites possibly having higher energy. A distorted lattice or more surface dislocations might explain increased anodic dissolution.

Simnad and Evans and Greene and Saltzman found that the main factor explaining increased corrosion rate in hydrochloric acid
due to strain was a movement of the anodic polarisation curve, without change in polarisation (Tafel slope). The former authors regarded this as due to a lowering of anodic potential (for mild steel) by some 25 millivolts; the latter regarded the effect as due to an increased anodic exchange current density. Heavily slipped areas of wires strained in tension showed more marked local attack (38).

Windfeldt (39) actively strained annealed iron wires in tension while in dilute hydrochloric acid, and observed a potential drop of about 10 millivolts, which was independent of pH. The potential rose to near the potential of the unstrained wire after fracture, when plastic flow was no longer active.

However Foroulis and Uhlig (47) and Foroulis (48) (studying worked pure Fe-C, Fe-N, and Fe-C-Si alloys) concluded that hydrogen overvoltage was lower at imperfection sites (dislocations with Cottrell atmospheres) and thus the rate of the controlling cathodic reaction was increased. This may be peculiar to the systems studied. Pure iron showed no difference in corrosion rate, cold-worked or annealed.

With regard to the effect of plastic strain in neutral chloride solutions, it seems that the potential drop still occurs (irrespective of any damage to oxide films), but both strained and unstrained materials polarise to the same value (41), probably an effect of oxygen availability. Increase in corrosion rate, if both anodic and cathodic reactions are stimulated by strain, would result in little change in potential, as pointed out by Evans (46). More important than the direct
The effect of strain on potential or corrosion rate is the galvanic effect when strained steel is coupled with unstrained steel (49), or where stress variations occur. Even then, corrosion may not be increased because diffusion of oxygen is limited (43). However, definite stress-concentrations, especially if associated with pits or crevices, may increase the anodic reaction rate markedly, and this concept appears in stress-corrosion theories.

2.2.6. Atmospheric Corrosion. Corrosion under conditions of complete immersion only partly applies to the present work, and some aspects of atmospheric corrosion theory should be considered. The main factors, demonstrated by Vernon (50,51), need not be discussed in detail. A relative humidity exceeding about 65% is important, so that a film of moisture (with dissolved salts etc.) is present on the steel surface. Points of corrosion develop at discontinuities in the oxide film (52), and ionic transport in the moisture film rather than oxygen availability often controls the corrosion rate (15), so strain in the steel may affect corrosion rate more than for corrosion under fully immersed conditions in neutral aerated solutions.

The differential aeration cell under isolated droplets of water or solution is of particular relevance, the metal at the centre of the drop being anodic to the more aerated metal near the edge (53).

2.2.7. Effect of Steel Composition, etc. Alloying elements may be expected to alter the corrosion rate of steel in most environments, but under neutral saline conditions where the rate is controlled by
30.

oxygen diffusion in the solution, little effect is to be expected\(^{(44)}\). The data quoted by Uhlig\(^{(54)}\) and by Hudson\(^{(55)}\) show this to be so, for a number of low alloy steels. Alloying with chromium (about 3\%) does reduce the corrosion rate by slowing the anodic reaction, but only by a factor of 3. Similar remarks apply to atmospheric corrosion\(^{(55)}\).

Of more importance to the present work is the effect of structure (and hence composition, heat-treatment and "cleanness") on the distribution and mechanism of corrosion. Inclusions and anodic particles encourage pitting\(^{(25)}\), and cathodic constituents may serve to increase corrosion rate or in certain circumstances promote anodic passivation\(^{(23)}\). Carbides are cathodic to ferrite\(^{(201)}\), and in addition the hydrogen overpotential is low\(^{(56)}\).

### 2.2.8. Note on the Corrosion Properties of Cadmium

The standard electrode potential of cadmium is close to that of iron (Cd/Cd\(^{++}\) = -0.402 volts, Fe/Fe\(^{++}\) = -0.440 volts)\(^{(11)}\), but cadmium in neutral salt solutions is anodic to iron\(^{(13)}\). The Pourbaix diagram\(^{(13,14)}\) indicates that cadmium should not become passive in environments of pH less than 9, but it is readily chromated\(^{(57)}\). The chromate film inhibits corrosion, the mechanism involving a slow leaching out of chromate ions.

### 2.3. Hydrogen in Iron and Steel

#### 2.3.1. General Remarks

The detrimental effects due to, or attributed to, hydrogen in steel have been known for a long time (e.g., hair-line cracks in steel forgings\(^{(72)}\)), but the theoretical aspects have been worked out only in the last twenty years. The hydrogen
content of steel is usually quoted in parts per million (by weight) or ml.\(H_2\) per 100 g. steel (measured at N.T.P.), 1 p.p.m. being roughly equal to 1.1 ml./100 g. A few p.p.m. of hydrogen in steel can cause embrittlement.

In discussing the subject of hydrogen in steel, it has been kept in mind that only the characteristics relating to hydrogen embrittlement at room temperature are important to the present study. Smialowski's recent book\(^{58}\) gives a comprehensive account of the whole subject, and the books by Szczepański\(^{59}\) and by Cotterill\(^{60}\) also, although these give greater emphasis to the aspect of embrittlement. A number of interesting papers are collected together in the report of the 1961 Conference at Harrogate\(^{61}\).

The form in which hydrogen exists in iron and steel is not known for certain, but it is generally agreed that atoms or protons are dissolved interstitially, and that at lower temperatures a high proportion of the hydrogen may be concentrated in so-called "traps", often identified as voids in the structure.

Since hydrogen in steel exists in several forms, which may have different effects on properties and different mobilities, values for diffusion rates, solubilities, etc. must be accepted only with reference to the method by which they were determined. This applies particularly to data for temperatures below 200°C \(^{76}\), or certainly below 130°C \(^{68}\) and extrapolation of high temperature data to below these temperatures.
may be misleading. The temperature range below 200°C is called "moderate" in what follows.

The heat-treatment and state of stress of the steel are also important. For example, in connection with embrittlement, Adenis and Baldwin (62) consider "noxious" and "innocuous" states of hydrogen in Armco iron; the states may be interchanged by appropriate heat-treatments. Larger quantities of hydrogen are occluded by steel when stressed or cold-worked (63, 64, 67, 96-99) and surface condition can influence the uptake of hydrogen markedly (79).

2.3.2. Solubility of Hydrogen in Iron and Steel A number of investigators since Sievert (1911) have determined the solubility of hydrogen in iron. Blake et al. (65) have tabulated the data of a number of authors, for the temperature range 300 to 900°C. In this range, solubilities in ferritic low alloy steels are similar to the solubility in pure iron (67), or a little greater, carbon perhaps tending to retain the hydrogen (68). Results vary, but in general terms, the figure of 0.2 p.p.m. may be taken for 300°C, increasing to about 4 p.p.m. at 900°C. Solubility in austenite is relatively greater still, so that steel at lower temperatures may easily be supersaturated (135).

These solubility figures refer to interstitial hydrogen in equilibrium with hydrogen gas at 1 atmosphere pressure. Sievert's law is obeyed, with deviations below 400°C (63), solubility being proportional to the square root of hydrogen pressure. This implies that the dissolved hydrogen is in equilibrium with adsorbed or gaseous
atomic hydrogen, which in turn is in equilibrium with molecular hydrogen (58).

There are good reasons for believing that at moderate temperatures, below 130 - 200°C, practically no hydrogen remains in interstitial solution. This would explain why experimental diffusion rates are low, and why hydrogen embrittlement is observed at lower, but not at higher, temperatures. Hewitt did not find internal friction peaks which could be associated with interstitial hydrogen (66).

2.3.3. Location of Hydrogen in Steel: "Traps". Bastien (69) has discussed the location of interstitial hydrogen (probably H⁺) in the ferrite lattice. Tetrahedral sites are most likely and X-ray diffraction evidence suggests that protons are preferentially located on the (112) planes (69,70). Apart from such considerations, it is generally accepted that hydrogen in excess of that required to saturate the lattice is segregated or precipitated at various forms of defect or "traps". At room temperature, practically all the hydrogen would be in traps.

The possibilities, as summarised by Bastien (69), are:

- H⁺ segregated at vacancies and dislocations;
- H or H₂ at dislocation pile-ups, grain boundaries and sub-grain boundaries;
- H₂ in blowholes, blisters, cracks (i.e. voids).

In addition, Troiano (133,139,140) has proposed that interstitial hydrogen tends to diffuse to regions of high stress, particularly triaxial stress.

Discharge of hydrogen into voids from the supersaturated lattice is likely to produce very high pressures of molecular hydrogen,
particularly at lower temperatures. De Kazinczy (126), quoting Phragmén's (71) expression relating temperature, pressure and solubility gave the example that equilibrium pressures for 5 ml H₂ (NTP) in 100 g steel would be 17500, 10870 and 17 atmospheres at 20, 100 and 600°C respectively. However, considering that much of the hydrogen at room temperature is "trapped" in various ways, an equilibrium pressure of 1000 atmospheres is more likely (134), and in cold-worked steel where the void volume is large, pressures may not exceed 1 atmosphere in voids.

Iron is classified as an endothermic occluder of hydrogen; iron hydrides are not expected, nor is there evidence for them (102). However, hydrogen-rich constituents have been observed or inferred at elevated temperatures (72, 73, 76), and with regard to moderate temperatures, Smialowski, considering the results of permeation experiments, takes the view that an unstable hydrogen-rich "IA-phase" exists (ref 58, p.117). This phase could be regarded as a "trap".

Another example may be ε-carbide (section 2.3.9). Austenitic stainless steels may form an alloy hydride phase, hexagonal in structure, when cathodically charged with hydrogen (233).

2.3.4 Hydrogen Diffusion in Steel Rates of hydrogen diffusion have usually been estimated from rates of evolution of hydrogen from steel held at given temperatures in vacuo (73-77) or from the rates of permeation of hydrogen through steel membranes, hydrogen solubilities being known (73, 87). Sykes, Burton and Gegg (73) investigated the
evolution of hydrogen from steel billets at temperatures of 400°C and above. For the several steels used, the diffusion coefficients were similar. They noted that the time required to extract hydrogen from billets at room temperature was much longer than predicted by extrapolating high temperature data, and Hobson (74,75) doing similar experiments in the temperature range -78 to 200°C confirmed the low evolution rates, and showed that the rates depended on steel composition.

Johnson and Hill (76) reached similar conclusions, studying the evolution of hydrogen from nearly pure iron cylinders, charged with hydrogen, in the temperature range 25 to 780°C. The diffusion coefficients calculated from evolution rates were relatively low below 200°C, the values being expressed by the equations:

$$D = 0.0014 \exp(-3200/RT) \text{ cm}^2 \text{ sec}^{-1} \text{ above } 200°C$$

and $$D = 0.12 \exp(-7820/RT) \text{ cm}^2 \text{ sec}^{-1} \text{ below } 200°C$$

The apparently slow diffusion in the lower temperature range is easily explained if the evolution rate is controlled by the rate of removal of hydrogen from traps, and not by the rate of diffusion. Johnson and Hill postulated that the hydrogen was trapped with an energy of about 4.8 Kcal/g atom below that of interstitial hydrogen. In this connection, Hewitt (66) noted that internal friction peaks (in strained steel), which could arise from the interaction between interstitial hydrogen and dislocations or other traps, indicated an activation energy of the same order as that for the process controlling evolution at low
temperatures.

Permeation experiments through membranes pre-saturated with hydrogen, so that traps are filled and only interstitial hydrogen diffuses, give rather higher values for \( D \).

Examples of values obtained for \( D \) at room temperature follow:

<table>
<thead>
<tr>
<th>Steel Type</th>
<th>( D ) (cm(^2) sec(^{-1}))</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nearly pure iron:</td>
<td>(2.2 \times 10^{-7})</td>
<td>Evolution (76)</td>
</tr>
<tr>
<td>2% Ni-Cr-Mo steel:</td>
<td>(3.2 \times 10^{-7})</td>
<td></td>
</tr>
<tr>
<td>3% Cr-Mo steel:</td>
<td>(5.0 \times 10^{-8})</td>
<td></td>
</tr>
<tr>
<td>14% Cr steel:</td>
<td>(2.8 \times 10^{-9})</td>
<td></td>
</tr>
<tr>
<td>Pure iron:</td>
<td>(1.5 \times 10^{-5})</td>
<td>Predicted from high temperature data, ref. 73 and ref. 93 from data of ref. 76</td>
</tr>
<tr>
<td>Armco iron:</td>
<td>(8.3 \times 10^{-5})</td>
<td>Permeation (87)</td>
</tr>
<tr>
<td>AISI 4340, at UTS of 112-121 t.s.i.</td>
<td>(2.0 \times 10^{-7})</td>
<td>Permeation (87)</td>
</tr>
</tbody>
</table>

Diffusion rates depend on steel structure (77) and on stress-condition (67,98) as well as on composition.

2.3.5. Introduction of Hydrogen into Steel. Hydrogen is taken up by steel during manufacture, for example from atmospheric moisture during melting (73), or subsequently by heating in hydrogen-containing atmospheres (72), or during surface treatments by which hydrogen is discharged cathodically. Methods used in the laboratory to "charge" steel with hydrogen have been discussed briefly by Hobson and Sykes (78) and by Frohmberg et al. (132).

There are two techniques based on heating in hydrogen, designated
thermal charging and pressure charging by Johnson and Hill\textsuperscript{(76)}. The former involves high temperatures in the range 1200 to 1370°C\textsuperscript{(72,76,78)}, the latter moderate temperatures and high pressures, e.g. 600°C, 140 atmospheres\textsuperscript{(76,78)}. The hydrogen may be retained by water quenching\textsuperscript{(78)}. Cathodic charging techniques introduce hydrogen far in excess of that required to saturate the lattice. The main advantage is that the heat-treated condition of the steel is unaffected, but unless conditions are closely controlled, results tend to be erratic\textsuperscript{(78)}. For short charging times, the hydrogen is located near the surface, and inevitably a concentration gradient from surface to core will exist; however the hydrogen can be evenly distributed through the specimen by baking at 150-200°C after electroplating with cadmium to retard outgassing\textsuperscript{(142)}.

The surface reactions which may occur during absorption and desorption, and their kinetics, have been discussed by Hudson et al.\textsuperscript{(79)} and by Owe Berg\textsuperscript{(80,81)}, largely without the involvement of electrochemistry. The surface condition of steel, structure, cold-work are factors which affect the absorption of hydrogen from aqueous solutions, reactants being adsorbed on the steel surface.

To charge steel with hydrogen, it is common practice to make the steel cathodic in 4% sulphuric acid\textsuperscript{(77)}, to which may be added a "poison" to inhibit evolution of hydrogen gas and so promote hydrogen absorption\textsuperscript{(99,130,146)}. An alternative is cathodic treatment in sodium hydroxide solution\textsuperscript{(90)}, sometimes with sodium cyanide added\textsuperscript{(91)}. Hydrogen
is also taken up when steel simply dissolves in mineral acids (except nitric acid) \((79, 82, 97)\), and also when steel corrodes in slightly acid environments containing hydrogen sulphide \((69, 77)\).

The absorption of hydrogen during electroplating has been studied extensively. Zappfa and Haslem \((83-85)\) used an embrittlement test - a standard bend test of wire round a mandrel \((86)\) - as an indication of hydrogen absorption. They showed that most plating baths embrittled more than cathodic pickling, and that cyanide-type baths embrittled markedly more than most acid baths. Mild steel was relatively insensitive to embrittlement, but a hardenable stainless steel (possibly representative of hardenable steels in general) was embrittled by all processes.

Embrittlement, for a given steel, can be correlated with hydrogen uptake; for example, Devanathan et al. \((87)\) showed that permeation rates of hydrogen through membranes of Armco Iron and AISI 4340, under various cathodic treatments, could be related to mechanical properties. However, when different steels are considered, equal embrittlement (by any method of estimation) does not imply equal hydrogen uptakes.

The evolution of hydrogen gas is not necessary for embrittlement, as noted by Zappfa and Haslem \((84)\). The same point was made by Beck and Jankowsky \((88)\) in connection with experiments on ultra high strength steel (AISI 4340); hydrogen evolved as bubbles is obviously harmless.

The mechanism of hydrogen absorption has generally been assumed to involve an intermediate adsorption stage \((93)\), and this assumption is
Kinetic studies on iron electrodes are consistent with the existence of an equilibrium between adsorbed and absorbed hydrogen, the rate of absorption being proportional to the amount adsorbed. Evolution of hydrogen gas and absorption into the metal proceed from the same adsorbed state, and so are competing reactions. Cyanide ions are strongly adsorbed on a steel surface, and may increase hydrogen absorption either by blocking the highly active centres which catalyse the formation of hydrogen molecules or by weakening the bond between adsorbed hydrogen and metal.

The hydrogen absorption rate law may be linear or parabolic depending on whether the surface reaction is rate controlling (some chemical reactions) or not rate controlling (cathodic charging). The high concentration of hydrogen produced in the steel surface layers as a result of cathodic reactions was explained by Schuetz and Robertson by means of the concept of "fugacity", or virtual pressure of hydrogen gas (see also Darken and Smith), which can be related to hydrogen overvoltage:

$$E = \frac{2.3RT}{F} \log_{10}(f)^{\frac{1}{2}}$$

(R is the gas constant, T the absolute temp., F the faraday)

For an overvoltage, E, of 0.2 volts, fugacity, f, works out at about $10^6$ atmospheres.

There appears to be little data concerning the absorption of hydrogen by steels undergoing corrosion at room temperature in...
environments other than acids and sulphides, and in the absence of stress. Darken and Smith\(^{(97)}\) found that only traces of hydrogen were taken up from sodium chloride solution. However, under mild cathodic polarisation, steel will take up hydrogen from near-neutral solutions. Bolton and Shreir\(^{(94)}\) showed that a high strength steel, Rex.539, did not absorb hydrogen by simple immersion in an acetic acid/acetate solution of pH4, but at a cathodic overpotential of 50 to 200 millivolts hydrogen was taken up over a period of several hours. Less hydrogen was absorbed from a solution of pH6.

At very low current densities, such as used for cathodic protection schemes, (e.g. 1 to 100 ma/ft\(^2\)), the risk of hydrogen embrittlement is considered slight\(^{(95)}\). Bolton and Shreir used current densities of 0.1 to 0.25 ma/cm\(^2\) (100 to 250 ma/ft\(^2\)).

2.3.6. Effusion (Desorption) of Hydrogen from Steel The effusion of hydrogen from steel is controlled by the same equilibria as is absorption, and like absorption, desorption is sensitive to surface conditions, especially at moderate temperatures\(^{(79)}\). The process has been studied, or used, to eliminate embrittlement and to determine hydrogen contents and diffusion rates.

Hydrogen is evolved from hydrogen-charged steel during ageing in air at room temperature\(^{(72,77,83,99)}\), or faster by baking in air\(^{(72)}\) or boiling in water\(^{(77)}\). The evolution may be observed if the steel sample is immersed in mercury\(^{(67)}\).

For analytical purposes, hydrogen is usually extracted by
heating the steel in vacuo, at various temperatures (78, 94, 97). Both Darken and Smith (97) and Bolton and Shroir (94) found that most of the hydrogen introduced electrochemically could be extracted at moderate temperatures, but a residue required a higher temperature. Hydrogen already present in the steel seemed to be extracted mainly at the higher temperature. Although Bolton and Shroir considered that traces of moisture in the apparatus may have influenced the high temperature extract, the observations are consistent with a partial "trapping" of hydrogen, freshly introduced hydrogen being mostly mobile. If this mobile hydrogen is responsible for embrittlement (delayed failure under stress), de-embrittlement at moderate temperatures would be expected (94).

2.3.7. The Effect of Strain on Hydrogen Absorption There is little comment in the literature concerning the effect of elastic strain on hydrogen absorption, but the effect of plastic strain, e.g., cold work, has been well established (64, 96). The quantity of hydrogen occluded from the gas phase is considerably increased, and in addition to the normal endothermic process of occlusion, an exothermic mechanism of occlusion occurs in cold-worked material, possibly related to the chemisorption of hydrogen on internal surfaces.

The effect of cold work in increasing the amount of hydrogen entering steel from acids has been demonstrated by Darken and Smith (97), Hudson and Stragand (98) and Bastien (67). Seabrook, Grant and Corney (99) found
the same effect in connection with cathodic charging. Hydrogen penetrates more quickly into the strained steel (67), and the diffusion rate (as indicated by desorption rate) increases with increased cold work to a maximum and then decreases (98). Some of the hydrogen absorbed by cold-worked steel is difficult to remove again by baking, and permanent damage (blisters, cracks) may result (67).

2.3.8. Effects of Hydrogen on the Properties of Steel

Hydrogen, like any alloying element, affects most properties of steel to some extent. The most important effect, and the most relevant here, is a reduction in ductility, leading to a time dependent embrittlement. The characteristics of hydrogen embrittlement and the delayed failure phenomenon will be discussed in a separate section. Other effects are mentioned here.

Hydrogen has been reported to influence the transformations of alloy steels to some small extent (100), but the effects are not systematic, and there is some doubt concerning them due to the difficulty of isolating hydrogen effects from other factors (101).

Hydrogen has a marked effect on the damping capacity and internal friction properties of iron. Studies of these phenomena by Bastien and Azou (70) showed the importance of plastic deformation in connection with hydrogen embrittlement.

The effect of hydrogen on the yield point in iron has been reviewed briefly by Farrell (102), who concluded that interstitial hydrogen does not produce a low temperature yield point (in any case, interstitial
concentration is exceedingly low) and moreover, hydrogen in voids (Farrell's view) embrittles and thus may prevent yielding.

Hardness measurements must be made under conditions of slow loading of the indentor, in keeping with the time dependent characteristic of hydrogen embrittlement, in order to detect a hardness increase due to hydrogen.

Potential effects are relevant to the present work. Uhlig, Carr and Schneider (104) found that hydrogen dissolved in iron and iron-chromium alloys lowered their potentials in oxygen-free sodium chloride solution by as much as several tenths of a volt. They suggested that freshly pickled iron was active because of absorbed hydrogen. Zappe (105), discussing these observations, offered the explanation that the expansion of steel due to hydrogen concentrated in structural rifts was equivalent to cold-work (compare section 2.2.5.), and the rifts also constituted an increased area for chemical attack; work at Battelle had also shown an alteration in electrochemical potential. Patrick and Thompson (106), in a careful experimental study, showed that hydrogen in iron lowered the standard electrochemical potential (Fe/Fe^{++}) at least in the absence of oxygen.

2.3.9. Effect of Steel Composition and Structure on Hydrogen Behaviour in Steel. Most of the data relating to the effects of alloying elements on hydrogen in steel is for temperatures above 300°C (58), and is therefore not relevant here. For moderate temperatures, there are a number of observations and studies concerning susceptibility to
hydrogen embrittlement, and these are discussed in section 2.5.7. Greater susceptibility to embrittlement does not necessarily imply that the structure or composition has a greater ability to take up hydrogen; a smaller amount of hydrogen may be sufficient to embrittle, possibly because of greater inherent brittleness or notch sensitivity.

An example of this distinction is provided by the work of Bolton and Shreir (94). Rex. 539 absorbed hydrogen more rapidly and to a greater final quantity when tempered at higher temperatures under their experimental conditions, but it is well established that susceptibility to embrittlement is greater for higher strength levels (i.e., lower tempering temperatures).

Certain constituents of steel may have an affinity for hydrogen. Austenite, certainly, will dissolve more hydrogen than will ferrite, (2.3.2.) and so retained austenite is of importance. Other phases may interact with hydrogen, so falling into the category of "traps" at moderate temperatures; an example is γ-carbide, formed at low tempering temperatures in certain ultra-high strength steels (107). According to Reisdorf (107) it is likely to be an iron/silicon carbide; and according to Owe Berg (108) an iron/hydrogen carbide, Fe₂HC. However, the effect of carbon and carbide form in general on hydrogen occlusion appears to be small (63).

There is little information on the effect individual alloying constituents have on the diffusion of hydrogen. Data on apparent diffusion rates were given in section 2.3.4, for several steels.
Diffusion rates calculated from permeation experiments by Devanathan et al. (87), gave an interesting comparison between iron and an ultra-high strength steel; the rate of diffusion in the latter was about 1/400th of that in iron, which was taken to indicate that the solubility of hydrogen (interstitially) was 400 times greater than in iron. Bolton and Shreir (94) found that pure iron absorbed very little hydrogen under the standard conditions used for ultra-high strength steel.

Silicon is said to reduce the rate of diffusion of hydrogen in steel, and so reduce susceptibility to hydrogen embrittlement (109, 110), but see section 2.5.7.

2.4. Fracture of Steel

2.4.1. Crack Nucleation and Propagation. The fracture of metals involves two processes, crack nucleation (or initiation) and crack propagation. The energy requirement, and hence applied stress in the absence of other factors assisting fracture, is not necessarily the same for each. A metal is said to fracture in a brittle manner when no noticeable plastic flow occurs, and so whether "ductile" or "brittle" fracture occurs depends on the relative values of yield and fracture stresses, the latter involving shear and cleavage.

Cottrell (111) considers three distinct applied stresses in the process of fracture:

1. Yield stress, at which slip bands nucleate slip in other bands
2. Nucleation stress, at which slip bands nucleate micro-cracks
3. Growth stress, at which micro-cracks propagate to fracture.
In earlier proposed mechanisms, growth was assumed (in fact, or by implication) to be more difficult than nucleation, and most authors assume the prior existence of micro-cracks or other nuclei. However, according to Cottrell \(^{111}\), there is evidence that nucleation stress is greater than growth stress, and so for ductile fracture, yield stress must be less than growth stress.

Griffith's theory \(^{112}\) explains crack propagation fairly well. The material is assumed to contain micro-cracks ("Griffith's cracks"), and if, under the local conditions of stress, the release of elastic strain energy would be greater than the surface energy required to form new crack surfaces, the crack can propagate. A minimum crack length is required. The simple theory may be modified by other factors; e.g. Gowing \(^{113}\) pointed out that energy would be required for plastic deformation as the crack grows.

Crack initiation is usually assumed to be by stress-concentration, at a surface notch, groove or corrosion pit, or internally at a Griffith's crack, inclusion or lattice defect. Grain boundaries may present a weakness. The prior existence of micro-cracks in metals is doubtful, and several mechanisms for their production by pile-up of dislocations have been put forward, e.g. Petch \(^{114}\), Chang and Grant \(^{115}\).

Crack propagation may be stopped by yielding, i.e. by plastic deformation and work-hardening in front of the crack tip. The effect may be temporary, giving spasmodic crack growth, as in Edeleanu's mechanism for stress-corrosion \(^{193}\). A kinetic factor is involved, since if crack propagation is faster than rate of yielding, brittle
fracture may proceed, even although the growth stress exceeds the yield stress; a model for crack propagation, based on the dynamic-yield concept and crack velocity, has been derived by Hahn et al. (116) for the brittle fracture of mild steel.

2.4.2. Britteness in Steel. The various aspects of this subject have been reviewed by Szczepański (59). Steels show brittleness, i.e., reduction of ductility in tensile or cupping tests, or reduction of "toughness" in impact tests, under various circumstances. However only two such circumstances are of especial interest here, for comparison with hydrogen embrittlement:

(1) Iron and steel, in company with other body-centred cubic metals, has a brittle-ductile transition temperature (range). Below this, usually at sub-zero temperatures, brittle fracture occurs (117). Cleavage cracks develop after slight yielding (118).

(2) Tempar brittleness, developed by tempering alloy martensites at certain temperature ranges, is associated with the precipitation of networks or films of carbides or other compounds intergranularly (119-121). Banerjee (121) has recently made an electron microscope study of "tempered martensite embrittlement" and "temper embrittlement" of high strength steels (including AISI 4340) brought about by heating at 260°C and 482-538°C respectively, and has suggested a mechanism for both involving the precipitation of carbides at dislocation intersections and jogs at the lower temperature and a decrease in dislocation density and agglomeration of carbides above 482°C.
Embrittlement, or brittleness, is not a property that can be uniquely measured or defined, but depends on the method of test. Brittle fracture is more likely in the presence of notches or other stress-raisers, and this gives rise to the concept of notch-sensitivity of a steel \(^{(59,165)}\). Often a rapid rate of loading (e.g. impact) promotes brittle fracture, especially if dislocation movement is hindered.

2.4.3. Other Factors Promoting Brittle Fracture. From the above, it is clear that any factor that raises the yield stress or that facilitates cracking by providing nuclei, by lowering the energy requirement for crack growth, or by providing additional energy for the process, will promote brittle fracture. For example, corrosion pits may nucleate cracks, and preferential attack at the crack tip \(^{(181,208)}\) or the wedging action of corrosion products \(^{211,212}\) may assist crack growth.

Non-corrosive fluids may influence crack growth. The strength of glass varies with the liquid contacting its surface, and this has been attributed to an effect on the surface energy of the crack surface \(^{(122)}\), and a similar mechanism has been applied to metals \(^{(123,204)}\). The rate of growth (in a high strength steel) is also affected by the relative humidity of the atmosphere \(^{(124,231)}\).

Crack growth may be controlled by time-dependent changes in the metal, e.g. diffusion of interstitials, as in hydrogen embrittlement. Interstitials (e.g. carbon, nitrogen) may hinder yielding by locking dislocations \(^{(111,119,202)}\), so promoting brittle fracture.
2.5. Hydrogen Embrittlement

2.5.1. Introductory Note  The embrittlement of steel by hydrogen manifests itself in several ways, for example, the hair-line cracking of certain alloy steels, general reduction in ductility of steels charged with hydrogen, and the delayed failure of high strength steels under static load.

The formation of hair-line cracks (or "flakes") in alloy steels has been studied extensively, and has been shown to result from a combination of hydrogen introduced during steelmaking or subsequently and internal stresses derived from transformations during cooling. It appears that the cracks form only after the temperature has dropped below about 150°C. Hydrogen contents as low as 2 p.p.m. can produce loss of ductility and even hair-line cracks in susceptible steels. The cracking of welds due to hydrogen from moisture in the arc is a similar effect, and again the cracks only form after cooling.

Zappfe and Sims discussed and illustrated the various effects, and gave an extensive bibliography (from 1801).

The discussion which follows applies more particularly to the embrittlement (and delayed failure) of high strength steels by hydrogen taken up during cathodic treatments, although the theories described were often developed to explain hydrogen embrittlement generally. Very small quantities of hydrogen, freshly absorbed, give detectable embrittlement.

The characteristics of hydrogen embrittlement are presented
first, so that the theories can be discussed in the light of these characteristics.

2.5.2. Characteristics of Hydrogen Embrittlement. The characteristics of hydrogen-embrittled steel have been listed by Cottrell (60) and by de Kazinczy (126). The main points, which the theories have to explain, are as follows:

(1) Normal tensile tests are not sensitive to the embrittlement, and the shape of the true stress-strain curve is barely altered, but increasing hydrogen content results in progressive reduction of fracture stress and ductility (67, 99, 127, 132). Eventually, when fracture stress drops below the UTS, fracture occurs with negligible ductility.

(2) At slow rates of deformation, e.g., when the load is applied slowly or is sustained at a level below breaking stress (see 7, below), the embrittlement is more easily detected (128, 129). Seabrook, Grant and Corney (99) found, for mild steel cathodically charged, that "embrittlement" was a maximum at strain rates less than 5/minute, and fell progressively as the strain rate was increased. Similarly, normal hardness tests do not detect the effect of hydrogen (99); a special test at slow loading rate is necessary (103).

(3) The embrittlement is reduced or disappears at sub-zero and at temperatures above 150°C (67, 130, 146).

(4) On ageing at room temperature, or on baking (131), the embrittlement is reduced. (Recovery rates for ductility and activation energy have been determined by Ferrall and Quarrell (146).)
(5) A strain greater than the elastic or yield strain is required for embrittlement, at least of a mild steel\(^{(99)}\).

(6) Steel composition, structure, surface condition and stress affect susceptibility. With regard to the last, Hewitt\(^{(66)}\) has pointed out that a steel cathodically charged while under stress fails more rapidly than if the same charging treatment were given prior to stressing.

(7) The most important characteristic of hydrogen embrittlement in connection with the present work is "delayed failure" under stress. For testing purposes, the embrittlement is indicated by the time to fail of a test-piece at a constant stress. An unembrittled test-piece would not fail. This aspect of hydrogen embrittlement is discussed in section 2.5.4.

2.5.3. Mechanism of Hydrogen Embrittlement; Theories. Theories of hydrogen embrittlement have to explain (1) the location of hydrogen in unstressed steel, (2) how it moves about in unstressed steel (de-embrittlement on ageing) and in stressed steel (time-dependent aspect of embrittlement), (3) where the hydrogen is located and in what form when fracture is taking place, and (4) why embrittlement occurs at moderate temperatures only.

The theories have been reviewed by de Kazinczy\(^{(126)}\), by Bastien\(^{(69)}\), by Frohmborg et al.\(^{(132)}\) and by Morlet et al.\(^{(133)}\), each author adding to the existing theories from his own work. Other reviews include Hill\(^{(134)}\), Smialowski\(^{(58)}\), Szczepański\(^{(59)}\) and Cotterill\(^{(160)}\).
The early theories assumed that dissolved hydrogen could hinder slip in some way, causing embrittlement; these will not be considered. The starting point of the modern theories is the "planar pressure theory" of Zappfe (135, 136), who attributed the embrittlement to hydrogen discharged into voids from a supersaturated lattice. The very large pressures of molecular hydrogen built up within the voids would cause premature failure under an applied stress. Suitable voids must be assumed to exist; Zappfe suggested that they were spaces in the lattice resulting from a slight relative tilting of lattice blocks (mosaic structure). Crack nucleation depends, then, on the stress concentration due to applied stress and internal pressure, and crack propagation on the diffusion of hydrogen in the lattice and its continued evaporation into the growing void to maintain the requisite pressure of molecular hydrogen. At high strain rates or low temperatures, hydrogen diffusion would be too slow and a degree of ductility would return.

Bastien (69), to explain that the effect of hydrogen is not noticeable in the elastic range, (70) postulated that hydrogen moves with the dislocations during plastic straining, and is discharged into voids, particularly at stress concentrations. The binding energy between protons and dislocations is too low to lock dislocations, but sufficient for the bound protons to move with dislocations, except at high strain rates when the dislocations may "escape" from their proton atmosphere.

Some authors (134, 102) have objected to this theory on the grounds that there is no direct evidence that protons form "Cottrell atmospheres"
round dislocations. However, internal friction studies give some confirmation of proton-dislocation interaction.\(^{(66)}\)

De Kazinczy\(^{(126)}\), accepting the "planar pressure" idea, and the existence of voids in the metal structure, pointed out that energy provided by the expansion of hydrogen within a crack would contribute towards the energy requirement for propagation. He also pointed out that the theory is still applicable if the pre-existence of cracks is not accepted. Dislocation arrays (produced by plastic strain) may be considered instead, and discharged hydrogen could then stabilise the opened tip of the array and promote nucleation of a propagating crack.

Patch and Stables\(^{(128)}\), extending Orowan's explanation of the delayed fracture of glass\(^{(122)}\), took the view that the critical stress for crack propagation in steel was lowered by the adsorption of hydrogen on the internal micro-crack surfaces, so reducing the surface energy of the growing crack.

The above theories explain, at least qualitatively, the time and temperature factors of hydrogen embrittlement, in terms of the mobility of hydrogen. However, it is difficult to explain the removal of molecular hydrogen from voids (in planar pressure theory) on ageing, and further difficulties were found by Morlet, Johnson, and Troiano\(^{(133)}\), who investigated the effect of plastic strain on ageing characteristics of hydrogenated steel. They concluded that the hydrogen in solution was damaging, not the hydrogen in voids, the latter not being mobile. It was postulated that hydrogen concentrates in highly stressed regions, creating a
concentration-gradient in conformity with the stress-gradient. Maximum embrittlement is in the region of most severe triaxial stress, such as at the root of a notch.

Blanchard and Troiano\(^{137}\) applied Cottrell's theory of brittle fracture (crack formation by coalescence of two dislocations in a cleavage plane) to hydrogen embrittlement, assuming that hydrogen enhanced the growth of crack arrays by increasing their energy. They accepted that hydrogen concentrates at dislocations, assumed that when the concentration exceeds the solubility limit the free energy of the steel will be increased, and thus derived an expression for the energy (and hence stability or tendency to propagate) of a potential crack in the presence of hydrogen. The suggested explanation for the increased energy at the tip of a dislocation array, where hydrogen is concentrated, is that the electrons associated with the protons join the d-bands of the metal, so increasing the repulsive component of the atomic bonding.

2.5.4 Delayed Failure Mechanism

Many papers and reports have been written about the delayed failure of steels, especially in connection with the embrittlement of ultra-high strength steels after cathodic treatments. Plain carbon steels can show the same effect - the embrittlement of plated springs is well known - and Bell and Sully\(^{138}\) investigated the delayed failure of circlips of 0.9% carbon steel which had been pickled cathodically, noting that susceptibility increased with hardness.

The delayed failure of ultra-high strength steels (AISI 4340) has
been investigated comprehensively at the Case Institute of Technology. The work was summarised and discussed by Troiano \(^{(139,140)}\). Notched tensile test-pieces were used, similar to those used in the present work. The test-pieces were heat-treated to strength levels (UTS) of 90, 103 and 121 t.s.i., and cathodically charged with hydrogen under standard conditions. Sustained load tests on test-pieces aged for five minutes after charging \(^{(132)}\) showed that there was an upper critical stress above which fracture was immediate and a lower critical stress below which fracture was indefinitely delayed. The upper critical stress was a little lower than the notch tensile strength (NTS) of the uncharged steel. At stresses between the two critical stresses, static fatigue life showed a small stress dependence only, with a considerable scatter. This stress range depended on UTS, notch acuity (decreasing acuity narrowed range from both ends) and on the ageing time between charging and loading.

In further work \(^{(141)}\) crack growth was followed by heat-tinting and electrical resistance methods. Three stages were distinguished:

1. a high rate of crack growth through the hydrogen rich case;
2. a slower rate of growth, attributed to control by inward diffusion of hydrogen just ahead of the crack tip;
3. final rapid mechanical failure through essentially hydrogen-free core. The cracks originated just below the root of the notch, at the point of greatest triaxial stress, and grew radially inwards, often branching symmetrically.

Test-pieces in which the hydrogen was distributed uniformly by
baking after charging (cadmium being used to prevent desorption), showed an incubation period for crack initiation under sustained load. This was interpreted as the time required for hydrogen to diffuse to the region of high triaxiality and to reach a critical concentration. Interruption of the loading during the incubation period gave results consistent with a reversal of hydrogen diffusion (under a concentration gradient) when the stress was removed.

Similar conclusions were reached by Klier, Muvdi and Sachs from a study of fractures. A sharp notch acts as a Griffith's crack, but a "mild" notch results in crack nucleation at the point of maximum triaxial stress - cupic point - possibly coinciding with an inclusion. The crack propagates inwards, sometimes branching symmetrically at 45° to the plane of the notch (the direction of maximum shear stress). The cupic point is deeper for milder notches. For smooth test-pieces, a crack nucleus near or at the surface is assumed, the crack propagating with the diffusion of hydrogen.

The above ideas explain the more rapid failure of a test-piece charged while under load. Hewitt has pointed out that the hydrogen taken up would diffuse directly to stress-concentrations, whereas in the absence of stress, the distribution would be more uniform, and further time would be required for redistribution when the stress is applied.

The work at the Battelle Memorial Institute, under Elsea, on plain test-pieces charged while stressed, gave stress/time to fail relationships similar to those found by Troiano. (See several WADC Technical Reports, \(142\), \(109\)).
especially ref. (143), and the review report by Elsea and Fletcher (144).

Troiano (139) has commented that a high strength steel containing a measurable amount of hydrogen may be embrittled by absorption of hydrogen too small to be detected analytically. This suggests that hydrogen already present in the steel, presumably in "traps", plays little part in delayed failure phenomena (except, perhaps, by providing crack nuclei). Charging and ageing experiments with deuterium suggest that there is little interchange between electrolytically introduced and extraneous hydrogen (145). However Farrell (147) still considered the embrittlement to be related to hydrogen in traps.

2.5.5. Delayed Failure Fractures The appearance of the fracture surfaces is consistent with the two main stages of fracture, namely (i) crack propagation through the hydrogen-rich surface layers or under the control of hydrogen diffusion and (ii) mechanical failure of the reduced section. Thus the fracture shows a dark rim, of finer texture, and a whiter centre of rougher texture (notched tensile test-pieces in ultra-high tensile steel being considered). The rim may be even (141) or irregular (142) in thickness, or may be represented only by a semi-circular area to one side of the fracture (108). Fractures illustrated by the last authors, Klier, Mvudi and Sachs, are of particular interest, because of their resemblance to fractures described in the present work. Raised edges, or shear lips, were observed in addition to mirror surfaces associated with sub-surface crack nucleation, possibly at inclusions. Farrell and Quarrell (146) also noted bright areas of cleavage
round inclusions in hydrogen embrittled ultra-high tensile steel; apparently in mild steel, similar cleavages could not be associated with inclusions (147).

2.5.6. Cadmium Plating and Delayed Failure of High Strength Steels

Hydrogen absorption by steels during cadmium-plating has been referred to earlier, section 2.3.5. A most important aspect is the problem of embrittlement of ultra-high strength steels, and a vast amount of testing work has been undertaken by the aircraft companies and others with a view to finding "non-embritling" cleaning and plating procedures, or to minimising the embrittlement by further treatments.

For present purposes, only a few remarks need be made. Some cleaning treatments, such as anodic pickling, produce less embrittlement than others (e.g. work at Saunders-Roe (148), but after plating the effect of the pre-treatment is marginal.

The substantial removal of hydrogen after cadmium-plating, is made difficult since the cadmium hinders desorption of hydrogen from the steel. Ageing at room temperature is not effective, although an equally embrittled steel uncoated may recover within a few days (149). Even a few hours baking at 150°C results in no appreciable loss of hydrogen (142). The higher the strength level of the steel, the harder it is to de-embrittle effectively. The sensitivity of the test-method is important; a baking treatment may seem to relieve the embrittlement entirely, but a more sensitive test may indicate that a severe embrittlement remains (156). Brown (131), experimenting with notched
tensile test-pieces of AISI 4340 steel, cadmium-plated and baked at 177°C, showed that at a strength level of 127 t.s.i. UTS, 200 hours baking resulted in little recovery when the sustained load test was at 75% NTS, but when testing at 50% NTS recovery was apparent after 160 to 200 hours baking, and at 35% NTS after 60 to 80 hours. However, at 100 t.s.i. UTS, recovery was complete after 24 hours baking, testing at 50% NTS. The same broad conclusions have been reached by other investigators (for example, Troiano(139)), but details are not consistent since procedures (steel, strength level, plating thickness, test method) differ widely. Often the baking temperature has been 200°C.

The cyanide cadmium plating bath is clearly most embrittling (see section 2.3.5.), and acid baths, based on sulphamates, perchlorates and fluoborates (88,150,151,156) and ammoniacal baths based on amino-acids (152) result in less embrittlement, at least after a baking treatment. However in throwing power and covering power these baths are inferior to the cyanide bath, and adherence of the plate may be less. Modifications to the composition of the conventional cyanide bath have reduced plating embrittlement (153).

The importance of throwing power when notched test-pieces are used was pointed out by Klier et al (149). Poor throwing power reduces the hydrogen uptake at the notch-root, particularly when the notch is sharp. Also, hydrogen may be more readily evolved from the notch-root if the cadmium there is very thin (154), especially less than 0.00025” (155). Beck and Jankowsky (66) and more recently Hartgroves and Langstone (154)
have investigated the thickness of cadmium plating at the notch—roots of high strength steel test-pieces. (Geyer et al.\textsuperscript{156}) filled the notches of test-pieces with wax, cadmium—plated, tested without baking, and observed delayed failure).

The use of undercoats of other metals plated from non—embrittling baths, to act as a barrier to hydrogen from the cadmium bath, has been investigated with some success\textsuperscript{(88,151)}, and the use of cadmium plating itself, thin enough to allow ready de—embrittlement but thick enough to prevent hydrogen uptake on further plating has been suggested\textsuperscript{(139)}. The development of a technique for applying substantial cadmium coatings by evaporation in vacuum\textsuperscript{(157)} has given a non—embrittling alternative to electroplating. As an undercoat, vacuum evaporated cadmium does not always prevent embrittlement on subsequent electroplating\textsuperscript{(156)}.

2.5.7. The effect of steel composition and structure on susceptibility to hydrogen embrittlement. The term "susceptibility" requires definition, since in comparing different materials, the susceptibility might be assessed in terms of embrittlement produced either by a given treatment or for a given hydrogen uptake. The two are not necessarily the same, and from a practical point of view the former comparison is to be preferred. It is not always clear in the literature what is intended by "susceptibility" or similar terms; there is no agreed definition, nor test method and conditions under which embrittlement should be measured. A more easily de—embrittled material might appear to have a lower susceptibility. (For stress-corrosion, Azhoin\textsuperscript{(158)} measured
susceptibility in terms of two constants defining the hyperbola obtained by plotting applied stress against time for a visible crack to form). Susceptibility to embrittlement by hydrogen must involve susceptibility to hydrogen absorption, so that some of the remarks made in section 2.3.5 are of relevance here; for example the observations by Zappfe and Haslam that mild steel was relatively insensitive to hydrogen embrittlement, and that a martensitic stainless steel was particularly susceptible. Bastien found, for a 0.2% C, 1% Cr, 0.3% Mo steel, heat-treated to develop different structures of equivalent strength, that pearlite, bainite and fine spheroidal "carbide" were less susceptible to embrittlement by cathodic charging than other structures; martensite was most susceptible. Frohmberg et al. also found that bainitic AISI 4340 was somewhat less susceptible than tempered martensite of the same strength. Reasons may be that the structures obtained at the higher temperatures were near equilibrium or had greater plasticity or had less residual stress.

With regard to composition, Elsea and Fletcher commented that no particular alloying element consistently affects susceptibility. However, silicon seems to reduce susceptibility in ultra-high strength steels. Klier et al. tested a number of commercial steels and concluded that they could be grouped as silicon-rich and silicon-dilute, and at high strengths, the silicon-rich steels were the less susceptible. Cheng compared three high strength steels of similar composition apart from silicon (0.30, 0.62, 1.40%), and found that their
resistance to plating embrittlement was in order of silicon content. The explanation may lie in the effect of silicon on diffusion rate or on $\varepsilon$-carbide (239).

Austenitic steels are little embrittled even at high hydrogen contents (67) and steels whose structure can be austenitic or ferritic according to heat treatment show much reduced susceptibility in the austenitic form (137). Whitman and Troiano (159) have summarised the information concerning the hydrogen embrittlement of austenitic steels. The greater tolerance of the austenitic structure for hydrogen gives rise to the suggestion, not well supported, that delayed failure in high strength steels may be due to the release of hydrogen during slow transformation of retained austenite (e.g., Hoyt (160)).

From the practical point of view, it has been said that only high strength steels at strength levels exceeding 80 t.s.i. are susceptible to embrittlement by plating processes, etc. (139); the higher the strength level, the greater the susceptibility and the more difficult it is to de-embrittle (131). However springs require de-embrittlement after cadmium-plating (138), and even mild steel screw wire may be embrittled (161).

2.5.8. Testing for Hydrogen Embrittlement. The types of test used for detecting and evaluating hydrogen embrittlement follow from the characteristics discussed in section 2.5.2. Absolute measurement of embrittlement is not possible, but comparative measurements can be made for example on the basis of loss of ductility - reduction in area in tensile tests, angle of bend to fracture in a slow bend test - or on the
basis of time to fracture in a sustained load test, usually with notched test-pieces.

A number of investigations have been made into the usefulness of various tests in evaluating hydrogen embrittlement. The rate of straining is important (see section 2.5.2.), and normal tensile tests are not sufficiently sensitive unless embrittlement is severe \(67,129,130\). The bend test is useful \(131,138,149,150,162\), provided that the loading is slow, so that the cracks spread under the control of hydrogen diffusion \(162\); otherwise, the cracks spread ahead of the hydrogen, and the rate of propagation becomes independent of embrittlement (the situation where the hydrogen is concentrated near the surface being envisaged). Fatigue tests have proved unreliable for assessing hydrogen embrittlement. Surface finish and the presence of residual stresses affect the results (e.g. Wedder and Cooper \(163\)). The reason is that the rate of loading is too rapid, surface cracks forming in the first few cycles and then spreading at a rate controlled not by hydrogen but by load and notch-brittleness of steel \(162\). Impact tests do not detect hydrogen embrittlement \(128,149\).

Sustained load tests are generally regarded as most sensitive \(131,149,162\) and notched tensile test-pieces have commonly been used \(88,109,110,141,142,148,151-156\), loaded in numerous devices. Alternative test-pieces are rings and C-rings, with notches \(151\) or drilled holes \(153\) as stress raisers, and to imitate more practical conditions bolts have been passed through holes in blocks, and the nut tightened to a standard
torque. Un-notched test-pieces have been used (84, 88, 131, 150), but they lack the sensitivity to small amounts of hydrogen.

Notch acuity is an important factor affecting stress concentration (164), the position of the point of maximum triaxial stress, the notch-tensile strength, and the upper and lower critical stresses (132, 142) (section 2.5.4). Notches in tensile test-pieces are conventionally cut with an included angle of 60°, but there is no agreement concerning the most appropriate stress concentration factor or radius at notch root. The former has been varied from 1 to 10 (109), the latter from less than 0.001" to 2" (142).

Details of notched tensile test-pieces used by several investigators have been collected in Table II. Stresses have been converted to tons per square inch where necessary and the theoretical stress concentration factor, $K_t$, determined from the dimensions using published charts (164).

The interpretation of notched tensile tests used to compare the susceptibility of different steels or structures to hydrogen embrittlement (or stress corrosion) must be made with care, since, as Brown has pointed out (165), the notch sensitivity of the steel may affect the results. However most investigators assume that a more rapid failure under test simply indicates greater susceptibility.
TABLE II

Some Details of Notched Tensile Test-pieces used in Hydrogen Embrittlement Studies.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Diameter, in.</th>
<th>Shank</th>
<th>Notch radius, in.</th>
<th>Notch root radius, in.</th>
<th>Stress concn. factor, $K_t$</th>
<th>UTS, t.s.i.</th>
<th>NTS, t.s.i.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 4340</td>
<td>0.300</td>
<td>0.212</td>
<td>0.002</td>
<td>0.004</td>
<td>6.4*</td>
<td>125</td>
<td>140.5</td>
<td>Jankowsky (68, 151)</td>
</tr>
<tr>
<td>AISI 4340</td>
<td>0.300</td>
<td>0.212</td>
<td>less than 0.001</td>
<td>more than 8.8</td>
<td>101.3</td>
<td>136.7</td>
<td></td>
<td>Barnett and Troiano (141)</td>
</tr>
<tr>
<td>AISI 4340</td>
<td>0.300</td>
<td>0.212</td>
<td>0.001</td>
<td>0.010</td>
<td>8.8</td>
<td>103</td>
<td>134</td>
<td>Frohmberg, Barnett &amp; Troiano (132)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>and Johnson, Morlet and Troiano (142)</td>
</tr>
<tr>
<td>AMS 6427</td>
<td>0.354</td>
<td>0.250</td>
<td>0.010</td>
<td>3.2</td>
<td>147</td>
<td>159</td>
<td></td>
<td>Reavey (148)</td>
</tr>
<tr>
<td>AMS 6407</td>
<td>0.354</td>
<td>to</td>
<td>to</td>
<td>0.003</td>
<td>to</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AMS 6418</td>
<td>0.250</td>
<td>0.21</td>
<td>0.010</td>
<td>2.8</td>
<td>147</td>
<td>159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>En. 26</td>
<td>0.25</td>
<td>0.21</td>
<td>0.010</td>
<td>2.8</td>
<td>147</td>
<td>159</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.250</td>
<td>0.1768</td>
<td>0.004</td>
<td>4.3*</td>
<td>Lockheed pattern</td>
<td></td>
<td></td>
<td>Carlisle (153)</td>
</tr>
<tr>
<td></td>
<td>0.250</td>
<td>0.175</td>
<td>0.003</td>
<td>4.9</td>
<td>McDonnell pattern</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*K_t from dimensions of test-piece, from Peterson's chart (164).

Jankowsky gives values of 6.0 and 4.2 for his test-pieces.

Carlisle gives $K_t = 3.9$ for average of notch root radii.

** Tons per square inch, in most cases converted from pound per square inch.
2.6. **Stress-Corrosion**

2.6.1. **General Features.** The term "stress-corrosion cracking" (SCC) implies fracture of a metal under the joint action of static stress and corrosion, the extent of damage being greater than expected from the effects of stress and corrosion separately. The phenomenon has been widely studied, and there have been a number of Symposia on the subject (166 to 169). Dix (190), and more recently Perkins (170), have reviewed the field, and a number of shorter accounts and general discussions of stress-corrosion are available (16, 25, 171 to 175).

Fracture may be accomplished with little overall corrosion attack, and material normally ductile may fail in an apparently brittle manner. Conditions under which stress-corrosion cracking occurs are often highly specific with regard to the corrodent, the alloy composition and structure, and temperature range. The simple explanation is that corrosion conditions must be borderline (e.g. between active and passive) for stress to affect the mode of attack significantly (172).

If general corrosion occurs, stress-corrosion is less likely. In several cases it has been shown that the potential across the metal-solution interface should be such that only the strained metal at the crack-tip actively corrodes (16). If the potential is made more anodic, such that general pitting occurs, stress-corrosion may not occur (176).

With regard to susceptibility to stress-corrosion cracking in an appropriate environment, Barnatt (174) makes the following points:
Pure metals are immune (SCC could be taken as evidence of impurity).

Homogeneous alloys, even rigidly purified, may be susceptible.

Corroding conditions, for SCC or immunity, are specific.

Minor constituents of an alloy can determine immunity or otherwise.

Heat-treatments, by changing structure, can determine immunity or otherwise. Internal stress condition may be critical.

Stress-corrosion may be intergranular (Evans said usually so), or transgranular. The latter is common in austenitic stainless steels and copper alloys. In some systems, the mode of cracking depends on pH of the corrodent or on structural condition (heat-treatment) of the alloy. Scheil has pointed out that intergranular cracking may be confused with ordinary intergranular corrosion.

A number of stress-corrosion systems have been studied in detail (examples are given in the next sections), and conclusions based on one system need not apply to all. Hence generalisations, as quoted above, must be accepted with caution. On the whole, they have been based on stress-corrosion studies of ductile alloys. Harder materials are more likely to fail by stress-corrosion, since stresses are less easily relieved by plastic deformation, and in particular, high strength alloys (the subject of this present work) do not fit the generally accepted SCC pattern of behaviour in several respects (e.g. closely specific corrosion conditions are not necessary), so that in the sections that follow high strength steels have been treated separately.
2.6.2. **Examples of Stress-Corrosion Systems.** It is not proposed to discuss alloy/corrodent combinations in detail, but merely to refer to a number of well-studied systems which give insight into the mechanisms involved in stress-corrosion cracking, and to indicate the scope of the subject.

1. Brass in ammoniacal environments (season cracking) \(^{(166,178,194,204)}\).
2. Aluminium alloys (e.g. Al-7% Mg) in chloride solutions \(^{(25,179,192)}\).
3. Magnesium alloys (e.g. Mg-7% Al-1% Zn) in chloride/chromate solutions \(^{(180)}\).
4. Low alloy steels in hot strong alkalis (caustic cracking, e.g. in boilers) \(^{(171,172,204)}\) and in hot strong nitrates (nitrate cracking) \(^{(171,172,197-203)}\).
5. Austenitic stainless steels in hot hydroxide or chloride solutions (e.g. boiling 42% magnesium chloride) or superheated steam \(^{(181,182)}\).
6. Low alloy steels (especially high tensile) in sulphide environments (sulphide corrosion cracking, e.g. in "sour" oil wells) \(^{(183-185)}\), and in cyanide solutions. Also austenitic stainless steels in geothermal steam \(^{(186)}\).
7. Martensitic stainless steels \(^{(186-188,219,233)}\) and high strength low alloy steels in various environments (see section 2.6.4).

2.6.3. **Stress-Corrosion Mechanisms and Theories.** A successful theory of stress-corrosion must explain how the conjoint action of stress and specific corrodents gives rise to crack initiation, often after an incubation period, and crack propagation through a ductile metal.
with little or no yielding. Corrosion alone may set the conditions for crack initiation in some cases, the level of stress during the incubation period being unimportant. However crack propagation does not occur, or will stop, in the absence of stress, or if the environment is removed, or modified, for example by de-aeration in the case of aluminium alloys. Crack growth in stainless steels, mild steels, etc., may be stopped by cathodic protection; propagation proceeds on removing the applied potential.

Crack path and crack propagation rates must also be explained.

Difficulties regarding the idea of brittle fracture may be overcome if the distinction made by Bates and Longinow between true mechanical brittle fracture and stress-corrosion fracture where yield occurs continuously at the crack tip is accepted.

In general terms (e.g. Robertson and Tetelman's "unified mechanism") stress-corrosion cracking requires a structural path of higher chemical activity and a mechanism for concentrating stress across that path. Chemical or other energy can provide additional energy for crack propagation. The detailed mechanisms proposed for each system will not be given here; such a discussion would not be relevant to the present work. However a brief account to illustrate the types of mechanism applicable to the ductile metals, and which may apply to high strength steels, is not out of place. (Mechanisms involving hydrogen are discussed in section 2.6.5).

Where grain boundary, or other continuous phases, are definitely
anodic to the matrix, continuous electrochemical attack is an obvious mechanism, (190) tensile stress assisting to localise the attack to suitably oriented sensitive paths (25). Such mechanisms formed the basis of the earlier theories, of Dix (190) and others (191,192), and are applicable to intergranular cracking of aluminium alloys.

More detailed studies, particularly of the transgranular cracking of stainless steel and some copper alloys, showed the need for other mechanisms. A second group of theories was based on the idea of alternate corrosion and mechanical steps. Simply, mechanically strong material might be destroyed by chemical attack, and less reactive regions mechanically fractured (25). In more detail, mechanisms have been developed, backed up by experimental evidence, whereby a slow anodic attack initiates a crack in some way, and the crack then propagates rapidly until it is stopped by yielding material or otherwise. Anodic attack of the disordered material at the crack tip then initiates a further crack. The mechanism of Edeleanu (193) and Forty (194), particularly for α-brass, is an example. (The periodic mechano-electrochemical mechanism was first proposed by Keating (195).)

Intermittent test-piece extension has been observed by Edeleanu (192) for aluminium alloys and by Hoar and Hines (180) for stainless steel wire, although there is some doubt attached to the latter (Hoar (16)). Recently, West and Fairman (196) could not detect intermittent extension of stainless steel, but Logan et al. (209) showed small mechanical steps fractographically.

Intergranular fracture in systems where the grain boundaries are not
definitely anodic to the matrix has been explained by a weakening of surface films at stressed grain boundaries when the combination of temperature and corrodent concentration provides borderline passive/active conditions. Caustic cracking and nitrate cracking of mild steel may be in this category. Engel and Bümel\(^{(197)}\) showed that boundaries could remain active when grains were passive in nitrates, and that potential deflections accompanied crack formation. Smialowski and co-workers\(^{(196-200)}\) also associated nitrate cracking with passivation phenomena, but Uhlig and co-workers\(^{(201-202)}\) preferred a mechanism called "stress-sorption cracking"\(^{(201)}\), based on the preferential adsorption of nitrate ions at grain boundaries sensitised by the segregation of carbon and nitrogen under the appropriate heat-treatment. Lowering of lattice bonding by adsorption at the crack-tip is assumed. Bonodicks\(^{(204)}\) earlier had taken a similar view of caustic cracking and season cracking, by analogy with the effect of moisture on the fracture of glass.

Transgranular cracking may be explained similarly. Pre-existing sensitive paths might be lattice defects\(^{(189)}\) to which solute atoms might segregate under the influence of stress and dislocation movements\(^{(205)}\). Many theories prefer to explain the formation of a path as the crack progresses, by anodic activity at the crack tip, which may alternate with slip or other mechanical crack mechanism, or by stress-sorption cracking.

Anodic activity has been explained by protective film rupturing\(^{(170,206)}\).
by yield-induced phase changes or by the high anodic current density supported by yielding metal. These ideas could apply to both inter- and trans-granular cracking; they require ductility rather than brittleness.

The stress-sorption theory, according to Uhlig, explains the specific effect of certain ions better, but potential measurements favour an electrochemical mechanism, and might even provide a method of estimating stress-corrosion susceptibility.

However Coleman et al., suggesting a common process — adsorption to explain similarities between stress-cracking under the influence of hydrogen, corrosion and liquid metals, pointed out that the observed electrochemical effects in SCC could relate to conditioning of the surface or of the electrolyte during the induction period.

A further mechanism suggested by Pickering et al., following Nielson, derived additional stress from the wedging action of corrosion products in the crack, and considered a capillary effect drawing corrodent into the opening crack.

Recent research on the stainless steels and other face-centred cubic alloys has been concerned with the correlation between stress-corrosion and the distribution, movements and interactions of dislocations. Thin-foil electron microscopy has shown the dependence of stress-corrosion susceptibility on dislocation network pattern and hence on stacking fault energy. An account of this topic has been given in Parsons' review, more briefly by Reed and Paxton, and the later
work has been discussed in papers by Tromans and Nutting (214) and Thomas, Stickler and Allio (215).

Crack initiation may occur on the stressed surface at sub-grain boundaries or grain boundaries, or at other active sites such as emergent dislocations (181) and stacking faults (215). Often corrosion pits at such sites or at no specified site have been accepted as stress raisers; linear arrays of pitting have been observed along certain lattice planes in thin foils (216).

The incubation period represents, then, the time required for the formation of pits or other features by corrosion (181), or alternatively for changes within the metal to develop active sites for preferential adsorption (217).

The above discussion has outlined a number of the mechanisms which have been suggested to explain stress-corrosion phenomena. The controversy which exists between rival theories, often both well substantiated, has been indicated. Some of the alternative explanations and theories may prove to be complementary and not mutually exclusive, but there are still great difficulties in producing a detailed mechanism applicable to all systems.

2.6.4 Stress-Corrosion of High Strength Steels Much less fundamental work has been done on the stress-corrosion of high strength materials, apart from certain light alloys. Perkins (179), in his review, paid no attention to high-strength steels, and the short account on high-strength steels in Shreir's book (ref. 6 page 846) deals mainly with hydrogen
embrittlenent.

High strength steels differ from austenitic stainless steels, ferritic carbon steels and other ductile materials in several respects regarding stress-corrosion. Brown\(^{(218)}\) listed four points of difference, comparing high strength steels with austenitic steels specifically:

1. High-strength steels crack readily at room temperature.
2. Specific ionic species in the corrodent are unnecessary for high-strength steels.
3. High-strength steels are susceptible to hydrogen embrittlement cracking.
4. High-strength steels are notch sensitive (and hence it is not necessary to explain brittle failure).

Brown, as other authors, distinguished between stress-corrosion cracking, a process based on the anodic reaction, and hydrogen embrittlement cracking, a process based on hydrogen absorption due to the cathodic reaction. Far less attention until recently has been paid to stress-corrosion of high strength steels than to hydrogen embrittlement, and much of the work has been directed towards the determination of the conditions under which cracking occurs, and of the relative susceptibilities of steels of different compositions and strength levels. Evidence has been sought as to whether the cracking should be regarded as stress-corrosion in the narrower sense or hydrogen embrittlement.

Cracking in acidic media, and in neutral or alkaline media under
cathodic polarisation, has usually been regarded as hydrogen embrittlement, analogous to the embrittlement arising from the acid pickling and cathodic cleaning of unstressed steels. As an example, Durkin's investigation of the behaviour of a stressed martensitic stainless steel in hydrochloric acid may be cited. Similar characteristics were observed whether the material was stressed after exposure to the acid or at the same time.

Sulphide cracking is a special case. The sulphide environment, often typified in the laboratory by acetic acid containing hydrogen sulphide, promotes hydrogen absorption. Most steels heat-treated to a hardness exceeding 24-26 Rc are susceptible. Frazier and Treseder proposed a mechanism involving a stress-corrosion step, the initiation of a crack at a stress-concentration (e.g., a pit) followed by a hydrogen embrittlement step — a Zappfe-type mechanism.

Hardness appears to affect the susceptibility to stress-corrosion more than does composition. This was shown by Bloom, mainly working with hardenable stainless steels. At hardnesses exceeding 24 Rc, cracking occurred in acetic acid/hydrogen sulphide solutions, but hardnesses exceeding 45 Rc were required for cracking in industrial atmospheres, salt fog or chloride solutions. In these tests, on unnotched U-bend and tensile pieces, cracks appeared to initiate in pits, were mainly transgranular, and resembled those obtained by cathodically charging stressed test-pieces with hydrogen. The low alloy steels tested, AISI 4130 and 4340, only failed in the acid sulphide environment; hardnesses did not exceed 36 Rc.
Little other work seems to have been done on the stress-corrosion of high strength steels in neutral salt solutions prior to the commencement of the present work. Samuel and Lockington (220) tested ultra-high strength steel notched tensile test-pieces (Rox.539), heat-treated to about 120 t.s.i. (about 55 R). Under sustained load, the incidence of failure of both coated and uncoated test-pieces was increased when they were sprayed with 3% sodium chloride solution. It was suggested that the corrosion process might release hydrogen during the test, particularly at defects in anodic coatings (cadmium, zinc) and thus contribute to hydrogen embrittlement failure. Stresses were about 70% of the notch tensile strength.

Phelps and Longinow (221) investigated the stress-corrosion cracking of various ultra-high strength steels, of both stainless and low alloy types. Plain strip test-pieces, bent in clips, were exposed to aerated 3% sodium chloride solution and to a marine atmosphere. AISI 4340, strength level 116.5 t.s.i., stressed at 50%, 75% and 90% of the yield stress failed in 12, 10 and 8 days respectively at Kure Beach.

Two investigations on ultra-high strength steels, heat-treated to strengths in the range 80 to 135 t.s.i., under stress in sodium chloride solution may be considered together. Davis (222) used strip test-pieces of AISI 4330 and 4340, stressed by bending to near the yield point. Hughes, Lamborn and Liebert (223,224) used En.26 steel in the form of cantilever test-pieces, and so were able to plot load against life. Higher strength level gave greater susceptibility, and in both
investigations, life depended also on the direction in which test-pieces were cut from the billet and on surface preparation. The curves of load against life were of the same form as for hydrogen embrittlement, and a lower critical stress was indicated for each condition of test\(^{(223)}\); the lives in the bend tests, however, showed considerable scatter\(^{(222)}\).

Cathodic and anodic polarisations were used during testing to obtain evidence regarding mechanism (for theory, see section 2.6.5.), and tests were also made in environments expected to promote hydrogen embrittlement\(^{(222)}\) - 0.25 N sodium sulphide\(^{(222)}\) and 0.1 N hydrochloric acid\(^{(223)}\). These tests indicated that in sodium chloride solution (without cathodic polarisation) a stress-corrosion rather than a hydrogen embrittlement mechanism applied. Life, plotted against potential\(^{(224)}\) showed a maximum to the cathodic side of the natural potential in sodium chloride (i.e. mild cathodic protection), and to the anodic side in hydrochloric acid; it was noted in both cases that the peak occurred near the appropriate reversible hydrogen potential. However fractographic studies, including electron microscopy, did not reveal any clear-cut difference between presumed stress-corrosion fracture and presumed hydrogen embrittlement fracture. The primary fractures were intergranular with respect to prior austenite boundaries.

Davis noted that under anodic polarisation in sodium chloride the crack tips were rounded, suggesting corrosion attack, but in sodium sulphide, with cathodic polarisation, sharp, fine cracks were produced. Hughes et al.\(^{(223)}\) noted subsidiary cracks on the tension face in
hydrochloric acid but not in sodium chloride solution.

Further work by Davis et al. (225), using notched test-pieces, correlated notch sensitivity with stress-corrosion cracking susceptibility, and showed that maximum susceptibility was obtained in the "500°F embrittlement" condition. Brown (226) has criticised the conclusions, on the grounds that the stress-corrosion tests measured a combination of SCC susceptibility and notch sensitivity, evidently regarding "susceptibility" in a narrow sense.

The recent investigation by Yamaoka and Wranglen (227), on AISI 4340 type steels stressed in water, demonstrated the sensitivity of the martensitic structure to stress-corrosion, paralleling its great susceptibility to hydrogen embrittlement (e.g. Bastien (69)). Tempering reduced the susceptibility, even to immunity, in the environment used.

Two very recent papers also concern AISI 4340 in the fully martensitic condition, stressed in 3% sodium chloride solutions at pH 1.5, 6.5 and 12.0. Toy (228) studied the effects of stress and aeration on polarisation curves under potentiostatic and galvanostatic conditions, and Tiner and Gilpin (229) the microprocesses (pitting, crack initiation, and fractography) occurring during stress-corrosion. The effect of tempering was only studied in the acid environment, so that the direct interest to the present work is limited. However for the untempered steel, the corrosion potential was about 0.1 volts more negative in de-aerated solution than in aerated solution. The effect of stress on corrosion potential varied with the conditions; for aerated neutral
solution, stress raised the potential by 0.04 volts. During the incubation period of stress-corrosion tests, minute cracks were observed just beneath the general surface at pits formed at sites of inclusions. These small cracks did not affect the tensile properties. They spread to the surface, and stress-corrosion crack propagation followed.

Examination of the stress-corrosion fracture surface under the electron microscope showed intergranular areas, mottled by iron dissolution, and transgranular areas, some dimpled, some flat (secondary cleavage) on which a tritium tracer was shown to collect. (These observations applied mainly, apparently, to stress-corrosion in the acid salt solution).

Tiner and Gilpin stressed the importance of \(\varepsilon\)-carbide in accelerating the cathodic reaction by absorbing hydrogen, and in locating the hydrogen in martensitic planes ahead of the crack. They noted that tempering, so transforming the \(\varepsilon\)-carbide to cementite, reduced the susceptibility very markedly. (Other structural changes, of course, occur during tempering).

The incubation period is generally accepted as much longer than the period of crack propagation. Tiner and Gilpin suggested that it occupied 14 minutes of a 15-minute life; Truman et al.\textsuperscript{(237)}, at least 72-89\% of the total life of martensitic stainless steels.

Life in the usual stress-corrosion tests includes an incubation period and a period during which the crack grows until rapid mechanical failure occurs. Identifying the incubation period as the time required
for a sufficiently deep pit to form. Brown and Beachem (230) eliminated it by using notched cantilever test-pieces precracked by fatigue. They deduced values for the threshold stress intensity below which stress-corrosion cracking does not occur, the values varying inversely with the strength level of the steel. The stress corrosion crack was assumed to grow until the critical stress intensity for mechanical brittle failure was attained.

However, Hanna, Troiano and Steigerwald (231), using pre-cracked test-pieces exposed while stressed to water or water vapour, found that there was still an incubation period before intermittent crack propagation proceeded. They attributed the embrittlement to hydrogen taken up from the water, time being required for hydrogen to accumulate at and just beyond the crack tip. The evidence for hydrogen embrittlement included the stress/life characteristics of the system, the effect of cathodic polarisation, and the reversibility of the incubation period with respect to stress (i.e., after temporary removal of stress, the full incubation time is still required). It is not clear whether a full recovery was achieved on removal of stress, which would be not easily understood, or whether recovery was only partial. (The steels were AISI 4340 and 300 M, at UTS 91 to 132 MPa).

The relationship between cracking time and stress has usually been treated empirically. However Azhogin (158) deduced from a consideration of relative corrosion rates at a stress raiser in the presence or absence
of applied stress that an equation of the form
\[(\sigma - \sigma_{\text{crit}}) \tau = k\]
should apply, where \(\sigma\) is the applied stress, \(\sigma_{\text{crit}}\) a critical or threshold stress, \(\tau\) the incubation period and \(k\) is a constant.
The values of \(\sigma_{\text{crit}}\) and \(k\) define the susceptibility of the system.
Experimental results for a number of systems were shown to fit the equation. High strength steels in acid environment, in hot neutral nitrate and caustic solutions were included, but unfortunately not high strength steel in neutral non-oxidising salt solutions.

2.6.5. Hydrogen and Stress-Corrosion. Theories attributing stress-corrosion cracking to hydrogen embrittlement are not confined to high strength materials, but mechanisms involving hydrogen have been suggested for most stress-corrosion systems. For example, Zappfe considered caustic cracking to be hydrogen embrittlement \((\text{105})\), and involvement of hydrogen has even been suggested for nitrate cracking \((\text{232})\). In the case of austenitic stainless steels in boiling magnesium chloride solution, Vaughan et al. \((\text{233})\) proposed that absorbed hydrogen diffused to stressed regions, precipitated a hydride phase, and thus provided a sensitive path for anodic stress-corrosion attack, during which stage the hydride would be destroyed. Snowden \((\text{182})\) suggested that the failure of martensitic stainless steels in boiling chloride solutions, when suitably tempered, might be due to hydrogen embrittlement.

The evidence of potential measurements on steels undergoing stress-corrosion is that potentials sufficiently low for the cathodic formation
of hydrogen are not attained in neutral media, at least in the cases of stainless steels in chloride solutions - Hear(16), and mild steels in nitrates - Smialowski(200).

A number of investigators have applied cathodic and anodic polarisation to stress-corrosion test-pieces, as indicated in the last section. The theory is that if corrosion, i.e. the anodic reaction, is primarily responsible for the fracture, anodic polarisation should stimulate the reaction and decrease life; cathodic polarisation should increase life of test-piece, conferring cathodic protection. If hydrogen embrittlement is the main factor, cathodic polarisation should stimulate and anodic polarisation reduce susceptibility to cracking. Phelps and Longinow(221) and Bhatt and Phelps(234) used this technique for a martensitic stainless steel (USS 12 MoV) in aerated 3% sodium chloride, and life, plotted against applied current, showed a sharp maximum just to the cathodic side of zero. The sharp decrease in life towards zero current then more slowly for an anodic applied current represents stress-corrosion cracking, and the somewhat slower decrease to the cathodic side of the maximum represents hydrogen embrittlement cracking (cathodic charging) (Fig. 28). An austenitic stainless steel, cold worked, gave similar results in sodium chloride solution containing hydrogen sulphide(188). The curves of Hughes et al.(224) for En.26 in sodium chloride solution, obtained under potentiostatic control, were similar although of somewhat different shape (see previous section).

Not all authors regard this type of evidence as conclusive, and have
looked for further evidence by comparing the crack characteristics with those where the mechanism is regarded as certain. Logan and Yolken (235) using notched mild steel test-pieces, compared stress-corrosion cracking under two very different conditions, namely in boiling 20% ammonium nitrate solution and in 1% acetic acid saturated with hydrogen sulphide. The first process produced pairs of intergranular cracks propagating intermittently in the directions of maximum shear stress; the second process produced a single transgranular crack and rapid failure.

Truman, Perry and Chapman (236) followed crack growth on the tensile surface of bent strip test-pieces, with a hole as stress-raiser, by means of a microscope. Martensitic stainless steels of various carbon contents were used, tempered at various temperatures, stressed in 3% sodium chloride solution or in acid environments. Polarisation experiments were included. The authors concluded that material tempered at high temperatures, above 450°C, failed by a predominantly active path mechanism, characterised by a multiplicity of branched cracks and fairly uniform rate of cracking, and that material tempered at lower temperatures failed by a hydrogen embrittlement mechanism — comparatively few cracks, relatively unbranched, discontinuous but rapid crack propagation after an incubation period. It was considered that the acidity in pits could rise sufficiently to make hydrogen evolution possible, even in neutral corrodents. Confirmatory evidence and further discussion has been provided by Truman, Perry and Peaker (237). Cold rolling, with the attendant structural changes, also affects the
relative susceptibilities of a steel to stress-corrosion and hydrogen embrittlement, as was demonstrated by Matsushima, Deegan and Uhlig (238) for a type 301 (17-7) stainless steel.

It is difficult to obtain definite evidence as to whether a hydrogen embrittlement is part of the stress-corrosion mechanism in neutral media, and the decision seems to depend on whether it is considered possible for hydrogen to become available. General hydrogenation of the metal is not proposed - only sufficient hydrogen concentrated at the crack tip, is assumed (236, 239, 240). Taking the evidence and opinions of various authors as a whole, it would seem that hydrogen embrittlement is not involved for quenched and tempered ultra-high strength steels, but for the same steels in the fully martensitic condition hydrogen embrittlement is quite likely (227, 229).

The experiments of Hanna et al. (231) were considered in 2.6.4.

Hydrogen can enter (and pass through) even a tempered AISI 4340 under stress from boiling sodium chloride solution as was shown by Logan and Wehrung (241), using an evacuated hollow test-piece; this information with the observation of internal brittle fracture initiation, is good evidence for hydrogen embrittlement. In the discussion following the paper, the authors said that similar evidence had been obtained at room temperature.

2.6.5. Effect of Surface Finish. The condition of the metal surface may affect the susceptibility to stress-corrosion in several ways. Blemishes of various kinds may provide stress-raisers, or provide
sites for pitting and so create stress-raisers. Surface stresses may be important, compressive stresses tending to reduce the effect of an applied tensile stress, and tensile stresses increasing the effect of the applied stress, or even being sufficient in themselves to initiate stress-corrosion cracks. Davis (222) showed the importance of surface preparation for ultra high strength steels. Techniques which tended to remove metal from the surface - grinding, electropolishing and chemical milling - increased susceptibility to cracking; techniques tending to make the metal surface flow - shot-peening, grit-blasting and face-milling - decreased susceptibility by introducing compressive stresses, and "sealing" defects.

2.6.7. Effect of Coatings Several investigators have included coatings in their work (1,185,220,221,242,243), but the only general conclusion is that some coatings decrease and some increase susceptibility to stress-corrosion, and some are unreliable. Silicone-base varnishes have been reported as effective barriers to corrodents (220,243).

The assessment of coatings is difficult, since their effectiveness depends on so many factors in addition to the intrinsic protective character of the coating material, e.g., the adherence of the coating, its ability to deform under stress, galvanic effects at coating defects, uniformity and thickness, state of stress in coating and in surface of substrate. Those factors in turn depend on the surface condition of the substrate, and on the care devoted to the coating process, which may itself introduce a hazard, such as hydrogen embrittlement. Finally, the
effectiveness of a coating may depend on applied stress-level \((243)\).

In view of the above, it is not surprising that there is no consistent body of information on coatings for stress-corrosion prevention. However the connection between electroplating and hydrogen embrittlement has been investigated very fully (see section 2.5.6) but again there are inconsistencies when details are considered.

2.6.8. **Stress-Corrosion Testing** The methods used for stress-corrosion tests and hydrogen embrittlement tests by sustained load are similar. Some methods have been indicated in the discussion of stress-corrosion above, particularly in section 2.6.4. The form of test-piece and apparatus depends on the type of data required and on the convenience of experimentation. Champion \((244)\) has illustrated a number of devices, classified as constant load and constant strain types. Flat strip test-pieces \((202,211)\) and horse-shoe test-pieces \((187,207)\), bent in some sort of clip to near the yield point, have often been used. They are simple, and the whole clip can be immersed in the corrosive. Wires, under tension \((181,192)\) and cantilever test-pieces \((223,230)\) permit a more accurate measurement of stress, but require more elaborate equipment. Machined tensile test-pieces \((220,225)\) need heavier equipment because of the higher loads for equivalent stress. Test-pieces are often notched to concentrate stress, and make the test more sensitive.

The test may terminate when the test-piece fractures, or at the first detection of cracks.
The corrosive environment may be applied to the whole rig or the test-piece only, continuously or intermittently (220, 222). Unless a particular environment is the object of the test, corrodents and conditions are normally chosen to produce fast cracking in susceptible members of the class of alloys in question, with little pitting or other corrosion attack. The addition of oxidising agents to chlorides, e.g., hydrogen peroxide (245) or chromates (246) is sometimes made to prevent pitting and so promote cracking.

Electrochemical tests have been recommended. Potential measurements between stressed and unstressed material in the corrosive environment can be used for a rapid indication of susceptibility (210). Impressed anodic currents, under potentiostatic or intensiostatic control may be used to accelerate a test or make it more specific (247, 249). Cracking may be accompanied by potential fluctuations (197).

In some stress-corrosion systems, very reproducible results can be obtained, e.g., stainless steels in boiling 42% magnesium chloride or pure iron in boiling calcium ammonium nitrate solution. Other systems, and in particular low alloy steels in chloride environments as in this present work, show considerable scatter in test-piece life, and the question of averaging results arises. Booth and Tucker (248, 249) have studied statistical life distribution, actually in anodically controlled tests on an aluminium magnesium alloy, and concluded that endurance was log-normally distributed and also that the geometric mean was the best representative value, the median being a good approximation.
2.7. Summary of literature with some Comments.

In the foregoing survey of the literature, the intention has been to set out, rather than criticise, the conclusions and opinions of investigators in fields relevant to the present work. A comparatively small part of the literature guided the experimental work; the greater part will prove useful in interpreting the results.

In the former category may be mentioned particularly the work on hydrogen embrittlement of high strength steels by Troiano and his co-workers (132) and the report by Brown (131) covering the characteristics of cadmium-plating embrittlement and the most suitable tests for its detection. Reference has been made to other papers on the same topics. The cracking of stressed ultra-high strength steel in neutral media seemed a new observation at the time; Bloom had failed to crack low alloy steels of lower strength (187), although he reported the stress-corrosion cracking of martensitic stainless steels in chloride solutions. Stress-corrosion systems of different characteristics were, of course, well known.

A summary of the more important points in the rest of the survey follows.

When steel corrodes in aerated neutral salt solutions, pitting is the normal mode of attack, and the cathodic reaction is the reduction of dissolved oxygen, the availability of which controls the corrosion rate. Although the over-all corrosion potential is not sufficiently low, hydrogen evolution has been observed (19), but only when the
solution is oxygenated so that corrosion can proceed actively. Although evolution may be exceptional, the first part of the reaction, to form adsorbed film of hydrogen, almost certainly occurs, polarising the cathodic areas unless removed. Cathodic depolarisation by oxygen or by, for example, chromate ions requires less energy than hydrogen evolution or hydrogen absorption by the steel, hence hydrogen absorption by steel from neutral solutions is not expected, and in fact only traces have been detected.

Carbides in a steel increase corrosion rate because of their low hydrogen overpotential, and stress increases both corrosion rate and the ability to take up hydrogen, at least in acid solutions. In aerated neutral solutions the effects are masked by the control imposed by oxygen diffusion on the system, but it is likely that the small part of the cathodic reaction resulting in hydrogen evolution or hydrogen absorption is increased. Plastic strain has a much more marked effect than elastic strain, especially when active, but the final corrosion potential is often little altered since both cathodic and anodic polarisation curves are affected by strain. Stress-concentrations are important, as they introduce potential differences between areas of differing stress.

Hydrogen may be introduced into steel from a number of sources. At around room temperature, hydrogen far in excess of the slight solid solubility may be absorbed as a result of electrochemical processes from acid solutions or under applied cathodic potential. Unless freshly
Introduced, the hydrogen is undoubtedly located in "traps", variously identified in the theories.

Hydrogen embrittlement was discussed at some length. The most distinctive characteristic is the "delayed failure" effect, and all the theories have explained this dependence of the embrittlement on time in terms of hydrogen diffusion through the lattice to the crack nucleus or propagating crack tip. The explanation of crack nucleation has often been avoided by assuming the pre-existence of micro-cracks or structural rifts, as in the planer pressure theories (85,135).

The suggestions that a "micro-crack" might really be a dislocation array (126) and that hydrogen is carried by moving dislocations (69) during plastic flow improved the theory in the sense that time is required for crack nucleation.

The studies of Troiano and co-workers of the delayed failure characteristics of hydrogen-charged notched tensile test-pieces of ultra-high strength steels established further characteristics not explicable in terms of the previous theories. The new theory assumed that when stress is applied, the hydrogen diffuses towards the region of greatest triaxial stress, just beneath the notch root, and becomes distributed in conformity with the stress gradient. Crack nucleation occurs when the hydrogen concentration is sufficient.

Embrittlement is considered due to mobile hydrogen, not hydrogen in traps. Crack propagation was shown to be controlled by the diffusion of hydrogen. The delayed failure period consists then of an incubation
period prior to nucleation and a propagation period. The theory explains
why temporary removal of stress during the incubation period results in
a further incubation period equal in length to the normal one; the
hydrogen diffuses back down the established concentration gradient
when the stress is relaxed\(^1\). The theory also explains why freshly
introduced hydrogen much less in quantity than that already in the steel
produces embrittlement, and why hydrogen absorbed by the stressed test-
piece causes more rapid failure than hydrogen absorbed shortly before
applying the stress\(^6\).

The stress-corrosion cracking of high strength steels differs in
several ways from the stress-corrosion cracking of more ductile materials,
and even among the latter it is unsafe to transpose the observations and
conclusions from one system to another, and even for a single alloy,
cold-work or heat-treatment may determine susceptibility or immunity.
The stress-corrosion of high strength steels in neutral salt solutions
has been studied by a number of workers, and attempts have been made
to distinguish between two broad mechanisms, hydrogen embrittlement
cracking and stress-corrosion cracking (taken to be a purely anodic
process). There would be little argument were it not for the known
susceptibility of these steels to hydrogen embrittlement.
Fractographic studies of test-pieces cracked under a range of conditions
have been inconclusive. Studies of the effect of imposed polarisations
on the time-to-failure appear to show that a SCC mechanism is more
likely\(^{2}\), although HEC may occur in untempered martensitic steel\(^{3}\).
The applied potentials or currents must be small, so that a mechanism is not imposed on the system; then the change in stress-corrosion life produced indicates whether the cathodic or anodic process dominates the cracking mechanism. An objection made to the simple interpretation is that the overall potential does not represent conditions in pits (236), or, presumably, cracks. A more important objection is that the fracture process takes place in at least two stages, namely an induction period leading to nucleation and a propagation period. Unless it is known which period is affected by the applied polarisation, the interpretation of the results obtained may be far from clear. Work with pre-cracked test-pieces (230, 231) is similarly open to objection; once a crack exists, its propagation might be facilitated by adsorption or other processes unconnected with the stress-corrosion mechanism occurring during the normal induction period.
3. EXPERIMENTAL INVESTIGATION

3.1. Materials and Test-pieces

3.1.1. Steels. Two steels were used in the investigation, specifications Rex.539 and En.40C. The former corresponds to the United States specification S.A.E.4340 (high silicon). Both steels were obtained as hot-drawn rod, \( \frac{3}{8} \) in diameter, of the following compositions:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Si</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rex.539</td>
<td>0.35</td>
<td>1.58</td>
<td>0.05</td>
<td>1.70</td>
<td>0.38</td>
<td>1.53</td>
<td>0.21</td>
</tr>
<tr>
<td>En.40C</td>
<td>0.36</td>
<td>0.55</td>
<td>3.33</td>
<td>0.26</td>
<td>0.91</td>
<td>0.28</td>
<td>0.15</td>
</tr>
</tbody>
</table>

These steels have been classified as "ultra-high strength steels" or "very strong steels", and are used as heat-treated and tempered to strengths of about 120 tons/square in. (t.s.i.).

3.1.2. Test-piece Design. The choice of notched tensile test-pieces for the stress-corrosion and hydrogen embrittlement tests was made after a short survey of published work and reports on hydrogen embrittlement of ultra-high strength steels. Such test-pieces have been commonly used, and are accepted as giving a sensitive indication of hydrogen embrittlement when subjected to a sustained load\(^{(131)}\). The stress-corrosion study was undertaken because of certain observations made during an investigation of hydrogen embrittlement phenomena\(^{(220)}\) and the same test-pieces seemed suitable.

The notched test-piece was derived from the standard No. 12 Hounsfield Tensometer tensile test-piece. The dimensions are given in Fig 1. The notch was cut more deeply than is usual so that the
notch-tensile strength (NTS) fell within the range of the Tensometer, which has a 2-ton limit; the cross-sectional area at the notch is 1/120 sq. in. The radius of 0.006" at the root of the notch gives a stress-concentration factor of $3.0^{(164)}$. (The stress-concentration factor, $K_C$, depends on test-piece diameter, notch depth, shape and acuity). Standard No.11 test-pieces were used for determination of other tensile properties (Fig.2.).

3.1.3. Machining and Heat-treatment. The test-pieces were machined from the rod to 0.030" oversize on diameter. They were then heat-treated to the required ultimate tensile strength (UTS), and finally machined to size, a tungsten carbide tipped tool, optically ground to a radius of 0.006" at the tip, being used to cut the notch.

The heat-treatment details were as follows:

Rex.539: Hardening, 850°C, 30 minutes, oil-quenched

Tempering, 350°C to 400°C for 2 hours, air-cooled

En.40C: Hardening, 940°C for 1½ hours, oil-quenched

Tempering, 250°C for 1½ hours, air-cooled

A small gas-fired natural draught furnace was used for hardening, and an electric tube furnace for tempering. Both furnaces were automatically controlled, the temperature being checked with a Pt-13% Rh.Pt thermocouple connected to an indicator with cold-junction compensation.

A range of tempering temperatures was used for Rex.539; the
FIG. 1 Notched Test-Piece Scale 4:1

FIG. 2 No. II Tensile Test-Piece Scale 4:1

FIG. 3
Shadowgraph of Notch Approx. x12
the corresponding range of tensile properties is given in Table III. The double-tempering treatment for En40C was recommended after tests by Fairey Aviation Ltd. (250) to avoid retained austenite.

3.1.4 Dimensional Check. The notch diameter of each test-piece was checked with a special gauge during machining. In addition, the test-pieces were examined with a microscope fitted with a 60 mm objective and a micrometer eyepiece, by means of which the dimensions of the notch could be measured, and the radius of the notch root calculated, assuming a 60° notch angle (see Appendix). Using the same objective with a projection eyepiece and camera, one test-piece of each batch was photographed. The effect was of a "shadowgraph", magnification about 12. By this means, the notch angle was checked. Fig. 3 is an example.

There was some variation in notch diameter, and the breaking load of individual test-pieces was calculated by multiplying the average NTS for the batch by the actual cross-sectional area at the notch. Tensometer tests confirmed that this was legitimate.

3.1.5 Determination of Mechanical Properties. The usual tensile properties and notch tensile strength were measured using a hand-operated Hounsfield Tensometer, points on the stress-strain curves being pricked out in the usual way. Tracings of typical curves are shown in Fig. 4. The maximum stress indicated was taken as the UTS.

Of each batch of 60 test-pieces, six No. 11 tensile pieces were made. Two of these were finish machined and tested as a check on heat-treatment before the rest of the batch was finished. The remaining
four represented each heat-treatment batch of 15 test-pieces. An extra test-piece was sent to Tensometer Ltd. occasionally, as a check on the accuracy of the tensometer.

The stress-strain curves for the notched test-pieces were straight, and terminated suddenly. The exact fracture stress was not easily observed, but could be determined by extrapolating the curve to the strain indicated by the final position of the rotating drum. This procedure is illustrated in Fig. 4.

The NTS (breaking load divided by cross-sectional area at the notch) showed some scatter, generally about ±2% for a batch of test-pieces. The average of four results was taken as the NTS for the batch of 60 test-pieces, unless excessive scatter made it desirable to break further test-pieces. Some batches were rejected for use in the main experiments. One reason for excessive scatter and low results was found to be the use of a worn notching tool.

The tensile properties of the batches of test-pieces are given in Table III. The batches used in the stress-corrosion tests have been given symbols (last column) by which they are identified in presentation of the test results. The low NTS for batch A1 is unexplained. This figure was reproducible for one of the earliest batches, and the stress-corrosion tests were completed before it was realised that the NTS should have been greater.

3.1.6 Stress relief The need for a stress-relieving treatment after final machining was investigated. Comparative stress-corrosion
### TABLE III

**Tempering Tests and Mechanical Properties**

<table>
<thead>
<tr>
<th>Tempering temp. C</th>
<th>NTS t.s.i.</th>
<th>UTS t.s.i.</th>
<th>Prop. L.t. t.s.i.</th>
<th>Rod. area, %</th>
<th>Elong. %</th>
<th>Ratio</th>
<th>Batch Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rex.539</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>1.57</td>
<td>1.09</td>
<td>1.00</td>
<td>45</td>
<td>1.3</td>
<td>1.44</td>
<td></td>
</tr>
<tr>
<td>390</td>
<td>1.56</td>
<td>1.13</td>
<td>1.03</td>
<td>46</td>
<td>1.4</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td>380</td>
<td>1.57</td>
<td>1.18</td>
<td>1.10</td>
<td>47</td>
<td>1.5</td>
<td>1.33</td>
<td>A1</td>
</tr>
<tr>
<td>380</td>
<td>1.70</td>
<td>1.19</td>
<td>1.09</td>
<td>46</td>
<td>1.2</td>
<td>1.45</td>
<td>A2</td>
</tr>
<tr>
<td>370</td>
<td>1.74</td>
<td>1.23</td>
<td>1.14</td>
<td>43</td>
<td>1.5</td>
<td>1.42</td>
<td>B</td>
</tr>
<tr>
<td>350</td>
<td>1.81</td>
<td>1.27</td>
<td>1.17</td>
<td>41</td>
<td>1.2</td>
<td>1.43</td>
<td>C1</td>
</tr>
<tr>
<td>350</td>
<td>1.77</td>
<td>1.27</td>
<td>1.19</td>
<td>43.5</td>
<td>1.2</td>
<td>1.39</td>
<td>C2</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>1.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>En.40C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300 twice</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 twice</td>
<td>1.66</td>
<td>1.23</td>
<td>1.08</td>
<td>42</td>
<td>1.4</td>
<td>1.35</td>
<td>D1</td>
</tr>
<tr>
<td>250 twice</td>
<td>1.60</td>
<td>1.23</td>
<td>1.07</td>
<td>46.5</td>
<td>1.3</td>
<td>1.30</td>
<td>D2</td>
</tr>
<tr>
<td>250 twice</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>**Stress-</td>
<td>1.69</td>
<td>1.22</td>
<td>1.02</td>
<td>38</td>
<td>1.4</td>
<td>1.39</td>
<td>D1</td>
</tr>
<tr>
<td>relieved**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**NOTES:**
- Tempering of Rex.539 was for 2 hours; air cooling.
- En.40C was tempered twice, each treatment for 1½ hours, cooling in air.
- The stress-relieving treatment was at 200°C for 20 hours.

(see section 3.1.6.)
and tensometer tests showed that the effect of such a treatment was slight, but since cadmium-plated test-pieces required a baking treatment at 200°C for 20 hours to alleviate hydrogen embrittlement (see section 3.5.3.) a similar treatment was given to most uncoated test-pieces also.

No significant change in tensile properties occurred in Rex.539, and the UTS of En.40C was reduced by not more than 1 t.s.i.

There seemed to be a slight increase of the NTS, especially for En.40C, of the order of 3 t.s.i. Since the NTS determinations were less reproducible than the other tensile figures, it was taken that no significant change occurred.

3.1.7. Hydrogen Content of Test-pieces. The hydrogen content of the finish-machined test-pieces was estimated by extraction at 600°C, using the technique briefly described by Bolton and Shreir (94). Triplicate results on the two steels were as follows:

Rex.539  0.10,  0.09,  0.10 ml. hydrogen per 100 g. steel
En.40C  0.12,  0.15,  0.13 "  "  "  "  "

(0.112 ml. H₂ per 100 g. is equivalent to 0.1 p.p.m. Barnett and Troiano's AISI.4340 contained 1.43 p.p.m. (141))

3.2. Apparatus - Sustained Load Rig.

3.2.1. General Requirements. The main function of the apparatus was to apply an axial load of up to 1½ tons on the test-pieces. The load should be known to a fair degree of accuracy, and be maintained for several weeks or months. The test-piece should be accessible, so that corrosives could be applied, and the development of corrosion...
products noted.

For convenience, Hounsfield Tensometer chucks should be used.

3.2.2. Description of Apparatus The original apparatus was described by Samuel and Lockington (220). This was modified later, but the principle remained the same. Calibrated helical compression springs were available, roughly 9\(\frac{1}{2}\)" long, 3\(\frac{3}{4}\)" inside diameter and 4\(\frac{3}{4}\)" outside diameter, and with parallel ends. These springs were individually calibrated before use on a hydraulic press, and deviations from the nominal 1" compression for \(\frac{1}{2}\) ton load, up to 1\(\frac{1}{2}\) tons, noted.

Fig. 5 is a photograph of a rig of the original design and Fig. 6 of a number of rigs of both original and modified designs. A diagram of the modified design is shown in Fig. 7. The main frame of the rigs was made from mild steel, largely protected by paint, and the central assembly (tension rods, nuts, chucks) from high tensile steels. The chucks were obtained from Tensometer Ltd. as standard parts. Other details of construction are given in sections 3.2.3. and 3.2.4.

The original design (see Fig. 2 of ref. 220) had a nut and washer in place of the ball-and-socket arrangement bearing on plate A, and the middle plate B was extended as a platform to take additional fittings if required.

3.2.3. Method of Loading The method is described with reference to Fig. 7.

(1) The test-piece was inspected for burrs or other defects at the shoulders (which could give rise to non-axial loads),
Fig. 5 (right)
Sustained load rig, original pattern.

Fig. 6 Set of rigs, showing original and modified designs. The coloured bands on the upper pillars indicate which corroden will be applied.
degereased with acetone and assembled in the chucks. (The notch had already been inspected — see 3.1.5.).

(ii) The chucks were fitted in the rig, the chuck pins being arranged at right angles to each other — as in Fig. 8.

(iii) With nut D clear of plate B, nut E was tightened by hand to take up the slack in the system.

(iv) The distance between plates B and C was measured, at three positions at 120° intervals round the spring. Internal callipers were used and a steel scale, the average of the three measurements, estimated to 0.01", being taken as the initial spring length.

(v) The desired load, generally 70% or 50% of the breaking load of the test-piece, was calculated, account being taken of the actual notch diameter, and the required spring compression read from the calibration graph.

(vi) The spring was compressed by tightening nut E with a long box spanner, the rig being horizontal. The ball-race and key-way at plate C prevented torque being applied to the test-piece. The number of turns given to nut E gave a rough indication of compression (12 turns were equivalent to 1"), and the accurate determination was made by remeasuring the distance between B and C at the same three positions. Any serious differences in compression at the three positions indicated poor alignment of the system. Nut D,
FIG. 7: SUSTAINED LOAD RIG — Scale $\frac{1}{3}$
Details of modified design.

FIG. 7A: Principle of Timing Device
A. Pivotted to bench
B. Rubber band
C. Contact
Fig. 8  Rod, Chuck, and Test-piece Assembly.

Fig. 9  Earlier Type of Rig.
clearing the plate by about \( \frac{1}{2} \), served as a stop when the test-piece fractured.

(In an alternative procedure, the spring could be pre-set, nut D, tightened against plate B, taking the load. Slackening of D then transferred the load to the test-piece, the slight relaxing of the spring being neglected).

(vii) The chucks, pins and test-piece except for the central \( \frac{3}{4} \) were lacquered by brushing with a cellulose product (Birlon Temporary Coating No. 2, Cellon Ltd.) as a protection against corrosion.

(viii) A simple circuit breaking device, stopping an electric clock when the test-piece fractured, could be attached to the (horizontal) rig. A light wooden frame rested on the bench under the rig, pinned to the bench as shown in Fig. 7A, and bridging the two rig plates B and C. When the test-piece fractured, movement of plate B was amplified by the wooden frame, and broke a contact consisting of a spring clip gripping a brass strip.

3.2.4. Advantages and Limitations of the Apparatus Some advantages of the type of rig used are as follows:

(1) The mechanism is simple and the cost low.

(2) Compared with a lever loading system, the space required is small.

(3) Hounsfield tensometer type test-pieces and chucks can be used.

(4) The spring deflection is large, measurable with a simple
scale to an accuracy of 2%. No strain gauges are required.

(5) The rigs can rest horizontally or stand upright without disturbance of the system.

(6) Fracture of the test-piece, and consequent movement of the centre-plate of the rig against the stop, is quite audible.

(7) This same movement (\(\frac{1}{4}\) in to \(\frac{1}{3}\) in) can be utilised in a very simple manner to break a circuit and so stop a clock.

(8) The test-piece is easily accessible, for observation and application of corrodent.

The main limitations of the rigs follow, with indications of the precautions taken to reduce their effect on the accuracy of the work:

(1) The ends of the springs tend to become non-parallel as the springs are compressed, with the consequent possibility of a non-axial (bending) load being transmitted to the test-piece.

It was considered unlikely that an unobserved non-axial load would be applied, provided care was taken in the operation of the rigs. Precautions taken were:

(a) All the springs had been used in very simple rigs, of the type illustrated in Fig.9, during earlier work. Springs which pushed the end plates out of parallel to a significant extent were not used for the stress-corrosion work.

(b) The support rods of the rigs controlled the tendency for the spring ends to go out of parallel.
(c) The chuck pins were arranged perpendicularly, so that small deflections of the system could be taken up.

(d) In the later models, the ball-end-socket joint, kept well lubricated (at A) could also take up small deflections of the plates.

(e) The method used for measuring spring compression gave immediate indication of the plates going out of parallel, and in practice any lack of straightness in the shaft-chuck-test-piece system was apparent by eye.

(2) A torsional load might be transmitted to the test-piece during loading. This was avoided by keeping the keyed shaft at the lower plate C and the thrust race between nut E and plate C in good condition. Any tendency to jam during loading was noted.

(3) Measurement of the spring extension at "no load", as datum for determination of compression applied, can be a source of error, more serious when the compression is small. However, for a given rig, the measured spring extension at "no load" proved reproducible to 0.5", representing a possible error of 2\% for a load of 1 ton. The behaviour of plain tensile specimens loaded in a rig confirmed the general accuracy of spring compression measurements.

3.3. Test Procedure

3.3.1. General Remarks. Since stress-corrosion tests were to be made on test-pieces which had been cadmium-plated and de-embrittled, it was necessary to distinguish between fractures arising from
residual hydrogen embrittlement and fractures attributable to corrosion. Earlier experience with hydrogen embrittlement had shown that "delayed failure" from this cause usually occurred within 3 or 4 days.

For the sake of uniformity of testing, all test-pieces (except those used for control purposes) were left under load for a week, before corrodent was applied. Failures occurring within the week were then attributed to hydrogen embrittlement or some other defect and subsequent failures to stress-corrosion. Later experience justified this (see sections 3.3.3.2. and 3.5.3.).

The term "corrodent" is used for any solution applied during the tests, irrespective of whether corrosion occurred. The time in hours, between first application of corrodent and final fracture of the test-piece is referred to as the "life" of the test-piece.

The rigs were placed horizontally or vertically on the bench as most convenient. Vertically, less bench space was used; horizontally, the corrodent could be applied to the test-piece more easily, and did not drain on to the chucks. In the course of the work (and other work not described here), it was found that test-piece life range was not affected by the orientation of the rigs.

3.3.2. Standard Test Procedure The test-pieces were loaded in the rigs, as described in section 3.2.3., and left for about 7 days. The corrodent solution was then applied once each day (excluding the two days of the week-end) until fracture occurred. If the rig was vertical
corrodent was sprayed from a small plastic bottle fitted with an atomising nozzle so as to wet the exposed central part of the test-piece. The preferred method was to allow a few drops of corrodent to fall on the notch of the horizontal test-piece, so as to wet the central part and leave a drop "hanging" to the notch.

In both procedures, the corrodent concentrated by evaporation and eventually dried. For horizontal test-pieces where the corrodent tended to drain to the lower part of the notch, while drying more quickly on the upper part, it was thought possible that fracture might be initiated preferentially at one of these positions. To confirm this, or otherwise, the heads of the test-pieces were marked with a scratch or groove so that test-piece orientation in the rig might be correlated with point of fracture initiation. (For comments, see section 3.7.4.)

In order that observations could be made during the first few hours, and that corrodent could be applied daily for as long as possible, the first application of corrodent was made for preference early on a Monday morning. Times of application of corrodent and of checking rigs were noted. Fractures occurring during the working day (8 a.m. to 6 p.m.) were audible, but for fractures occurring at night or during week-ends a timing device was used, or the time of fracture was taken to be 1 a.m. (i.e. midway between 6 p.m. and 8 a.m.). When tests were prolonged, exact knowledge of time of fracture was less important.

As soon as possible after the test-piece had fractured, it was
removed from the rig, rinsed, dried and examined.

3.3.3. Modified Procedures

3.3.3.1. Continuous Corrosion Procedure. With the rig horizontal, cotton wool was wrapped round the centre of the test-piece, and the ends dipped into a small beaker containing the corrodent.

(Results: See section 3.4.3.)

3.3.3.2. Control Tests In the course of the experiments, the standard procedure was varied in certain tests. The following variables were studied:

(1) The period on load before applying corrodent (1 hour to 8 weeks).

(2) The frequency of application of corrodent (twice instead of once daily).

(3) The NTS was determined after test-pieces had been on load for several weeks (with or without corrodent).

(4) Corrodent was applied for several weeks to the test-piece mounted in the rig with the spring pre-set (section 3.2.3, stage vi). The load was then transferred to the test-piece, and the application of corrodent continued or not.

(5) Ambient conditions (humidity, acid fumes or other contaminants, temperature) were noted qualitatively; no attempt was made to control these conditions, apart from shutting the door of the testing room.

The results of (1) to (4) are given in section 3.4.3., the last in section 3.7.1.
3.3.4 Corrodents (Solutions). The corrodents were made by dissolving the appropriate weight of the salt in a measured volume of distilled water. The concentrations below are expressed as \( \% \text{ w/v} \). The letters (a, b, c etc.) are used to identify the solutions.

(a) 3\% sodium chloride (laboratory reagent quality).

(b) Distilled water

(c) Tap water, hard, Uxbridge.

(d) 4\% sodium sulphate, anhydrous (laboratory reagent quality)

(e) 4\% potassium chloride (laboratory reagent quality)

(f) 5\% ammonium carbonate (commercial product, containing carbamates)

(g) 5\% potassium dichromate (analytical reagent grade)

(h) 5\% potassium chromate (analytical reagent grade)

(i) 3\% NaCl + 5\% ammonium carbonate

(j) 3\% NaCl + ammonium hydroxide to pH of (i) *

(k) 3\% NaCl + sodium hydroxide to pH of (i) *

(l) 3\% NaCl + 2.5\% potassium chromate

(m) 3\% NaCl + 5\%  "  "

(n) 3\% NaCl + 10\%  "  "

(o) 1.5\% NaCl + 5\%  "  "

* The pH was adjusted, using indicator papers; the value was 9.5 to 9.6.

3.4 Results of Stress Corrosion Tests (Uncoated Test-pieces)

3.4.1 Rox.539 Test-pieces (3\% Sodium Chloride Solution) Test-pieces were loaded at nominally 33\%, 50\%, 70\% and 80\% of their notch tensile strengths. At 33\% NTS, the life under stress-corrosion exceeded 8 weeks.
(1344 hours), but at 50 - 80% NTS, all except two test-pieces failed within 15 days. Detailed results are given in Table IV, grouped according to strength level (UTS) and applied load (% NTS). The same results are shown graphically in Fig.10, where the time scale is logarithmic.

In both tabulated and graphical presentations the results in each group are arranged in increasing order of test-piece life, and not in chronological order. These lives cover a wide range, not correlated at all with actual applied stress within each group, and it is because of the large scatter that the logarithmic time scale was adopted for the graph.

The small batch of test-pieces, B, at strength level 123 t.s.i., were wrongly stressed, as the NTS was wrongly determined. The stress-corrosion tests were under way before the corrected NTS was known. (The tensometer was at fault, and as this was the first batch tested, the error was not immediately obvious). The correct NTS and %NTS are given in the Table. Points on graphs relating to this set of test-pieces are bracketted.

The NTS has varied for different batches of test-pieces of the same UTS. This variation results in different applied stresses for a given %NTS (column 3 of Table IV). For this reason, in Fig.13 log (life) is plotted against applied stress, irrespective of NTS or UTS of the test-pieces.

3.4.2 En 40C Test-pieces (3% sodium chloride solution). The results
### TABLE IV
Stress-Corrosion Tests on Uncoated En. 40C in 3% Sodium Chloride Solution

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>110 t.s.i.</td>
<td>A1</td>
<td>75.3</td>
<td>48.0</td>
<td>0.4 *</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A1</td>
<td>75.0</td>
<td>47.7</td>
<td>0.9 *</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% NTS</td>
<td>A1</td>
<td>75.7</td>
<td>48.1</td>
<td>141</td>
<td>235</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>A1</td>
<td>78.0</td>
<td>49.6</td>
<td>145.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>85.5</td>
<td>50.3</td>
<td>240</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A1</td>
<td>78.5</td>
<td>50.0</td>
<td>206</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A1</td>
<td>74.0</td>
<td>47.1</td>
<td>103</td>
<td>* 302</td>
<td>* 254</td>
</tr>
<tr>
<td></td>
<td>A1</td>
<td>76.0</td>
<td>48.0</td>
<td>348</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| 127 t.s.i.              | C1    | 64.0           | 46.7       | 0.5 *                                           |                          |     |
|                         | C1    | 67.3           | 49.3       | 1.2 *                                           |                          |     |
| 50% NTS                 | C1    | 69.0           | 49.2       | 20                                              | 94                       | 30  | 125 |
|                         | C1    | 86.0           | 47.2       | 95                                              |                          |     |
|                         | C1    | 90.5           | 50.0       | 144                                             |                          |     |
|                         | C1    | 94.5           | 52.2       | 111                                             |                          |     |
|                         | C1    | 91.0           | 50.0       | 144                                             |                          |     |
|                         | C1    | 89.5           | 50.0       | 264                                             |                          |     |

| 110 t.s.i.              | A2    | 116.0          | 69.0       | 72                                              | 04                       | 03  | 05  |
| 70% NTS                 | A2    | 126.0          | 70.6       | 96                                              |                          |     |

| 127 t.s.i.              | C1    | 124            | 69.5       | 0.1 *                                           |                          |     |
|                         | C2    | 124            | 70.2       | 0.35 *                                          |                          |     |
|                         | C2    | 119            | 65.2       | 0.4 *                                           |                          |     |
| 70% NTS                 | C1    | 125            | 69.0       | 33                                              |                          |     |
|                         | C1    | 122            | 69.0       | 39                                              | * 94                     | * 65 | * 118|
|                         | C1    | 119            | 60.0       | 40                                              |                          |     |
|                         | C1    | 123            | 60.0       | 96                                              |                          |     |
|                         | C1    | 125            | 69.0       | 152                                             |                          |     |
|                         | C1    | 126            | 69.7       | 159                                             |                          |     |
|                         | C1    | 127            | 70.1       | 210                                             |                          |     |

| 127 NTS                 | C1    | 143            | 79.0       | 0.4 *                                           | 1.0                      | 0.9 | 1.1 |
|                         | C1    | 144            | 79.7       | 1.25                                            |                          |     |
|                         | C1    | 145            | 80.8       | 1.35                                            | * 1.3                    | * 1.3| * 1.3|

| 123 t.s.i.              | B     | 120            | 73.6       | 2.25 *                                          |                          |     |
|                         | B     | 132            | 75.9       | 40                                              | 176                      | 62  | 269 |
| (70% NTS)               | B     | 100            | 62.0       | 54                                              | 54                       |     |
|                         | B     | 103            | 59.2       | 64                                              | 2.25                     |     |
|                         | B     | 133            | 76.5       | 216                                             |                          |     |
|                         | B     | 131            | 75.3       | 672                                             |                          |     |
FIG. 10

Stress-Corrosion Life

REX.539 in 3% NaCl Solution
are given in Table V, and in Fig. 11. Tests were made at 50% and 70% NTS only.

3.4.3. Results of Some Control Tests (section 3.3.3.2)

(1) Test-pieces which were loaded at 70% NTS for 1 hour, 3 days, 14 days and 8 weeks before application of 3% sodium chloride had stress-corrosion lives within the same range as those tested in the standard way. (See also section 3.4.6.1.)

(2) More frequent application of corrodenent appeared to make no difference to the life of the test-piece, nor did the use of a cotton wool pad (as section 3.3.3.1.) make any clear difference to the life; a trend to shorter life is indicated in Table VIII.

(3) (a) Sustained load tests at 50 and 70% NTS for 8 weeks; no reduction in NTS was found, test-pieces breaking on the tensometer at 97 to 102% NTS (10 results). However when "inactive" corrodents were applied, some reductions in NTS were noted - see section 3.4.6.1.

(b) Stress-corrosion tests in 3% NaCl at 50 and 70% NTS; test-pieces removed after periods within the life-range but before failure showed no significant reduction in NTS, results being between 97 and 99% NTS. (When attempts were made to increase the stress from 50 to 70% NTS without removing test-pieces from the rig, failures occurred before or soon after the higher stress was reached).

Representative results are included in Table VI.

(4) Test-pieces to which sodium chloride solution had been applied before stressing showed no evidence of hydrogen embrittlement (by
### TABLE V

Stress-Corrosion Tests on Uncoated En.40C in 3% Sodium Chloride Solution

<table>
<thead>
<tr>
<th>UTS and Nominal Stress</th>
<th>Batch</th>
<th>Applied Stress</th>
<th>Life hours (icator of short life)</th>
<th>Life averages - hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ar. mean, &quot;Log. av.&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>RMS</td>
</tr>
<tr>
<td>123 t.s.i.</td>
<td>D1</td>
<td>83.0</td>
<td>50.0</td>
<td>0.1 *</td>
</tr>
<tr>
<td></td>
<td>D1</td>
<td>82.0</td>
<td>49.9</td>
<td>0.1 *</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>79.0</td>
<td>49.5</td>
<td>0.6 *</td>
</tr>
<tr>
<td>50% NTS</td>
<td>D2</td>
<td>80.0</td>
<td>50.3</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>80.5</td>
<td>50.3</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>D1</td>
<td>84.5</td>
<td>50.9</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>78.0</td>
<td>49.5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>D1</td>
<td>84.5</td>
<td>50.9</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>78.0</td>
<td>49.5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>D1</td>
<td>81.0</td>
<td>48.2</td>
<td>24</td>
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<td></td>
<td>D1</td>
<td>84.4</td>
<td>50.9</td>
<td>32</td>
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<td></td>
<td>D2</td>
<td>79.0</td>
<td>49.5</td>
<td>50</td>
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<td></td>
<td>D1</td>
<td>82.6</td>
<td>49.7</td>
<td>69</td>
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<td></td>
<td>D1</td>
<td>77.8</td>
<td>48.6</td>
<td>76</td>
</tr>
<tr>
<td>123 t.s.i.</td>
<td>D1</td>
<td>116</td>
<td>69.8</td>
<td>0.07 *</td>
</tr>
<tr>
<td></td>
<td>D1</td>
<td>113</td>
<td>68.0</td>
<td>0.1 *</td>
</tr>
<tr>
<td></td>
<td>D1</td>
<td>121</td>
<td>72.9</td>
<td>0.4 *</td>
</tr>
<tr>
<td>70% NTS</td>
<td>D2</td>
<td>109</td>
<td>68.2</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>112</td>
<td>69.3</td>
<td>1.9</td>
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<td></td>
<td>D1</td>
<td>111</td>
<td>69.3</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>111.5</td>
<td>69.7</td>
<td>18</td>
</tr>
</tbody>
</table>
FIG. 11.

Stress-Corrosion Life

EN.40C. in 3% NaCl Solution

Batches D1 & D2

Stress 50 70 % NTS

UTS: 123 tsi

LOG AVERAGE
LOG AV. excl. short lives
3.4.4. Comments on Results of Tests in 3% Sodium Chloride Solution.

Although there was a wide scatter in stress-corrosion lives, and no separation between life ranges at 50% and 70% NTS, some trends are apparent in the results. These trends, and other features, are pointed out below. Unless otherwise stated, remarks apply more specifically to Rex.539.

(1) For Rex.539, lives fall into two groups: short lives, of about 1 hour or less and lives longer than 24 hours. For En.40C, this distinction is much less obvious, since the gap between short and normal lives is smaller.

(2) En.40C lives are, as a whole, shorter than Rex.539 lives.

(3) Lives at 50% NTS tend to be longer than those at 70% NTS, both for short lives and longer lives. This is apparent from Figs. 12 and 13, life plotted against %NTS and actual applied stress respectively.

(4) At 80% NTS (Rex.539), lives are much shorter than at 70% NTS (or than at 75% NTS if the batch D results are considered). Although only three tests were made in the main series, there is no reason to classify these results as "short lives". Confirmation of greater sensitivity at 90% NTS was obtained from the tests on organic coatings. (See section 3.8.2.)

(5) At 33% NTS, lives were much longer; possibly, susceptibility to stress-corrosion is very low at this stress, or there may be no susceptibility.
FIG. 12
Stress-Corrosion Life against Stress — % NTS — for
REX.539 and EN.40C in 3 % NaCl

Batch A1 △ A2 ▲
B ●
Cl ○ C2 ●
D1 □ D2 □

Short Lives

APPLIED STRESS as % NTS
S. C. LIFE — hours
FIG. 13

STRESS-CORROSION LIFE against STRESS for
REX. 539 in 3% NaCl Solution

Batch A1 △ A2 ▲
B ◆
Cl ○ C2 ●

ACTUAL APPLIED STRESS — t. s. i.
3.4.5. **Average Stress-Corrosion Lives.** In order to obtain single figures for life at each applied stress and strength level, the average life (arithmetic mean) and "average log life" have been calculated for each group of tests. The latter is obtained by taking the arithmetic mean of the logarithms of the lives, and reporting the anti-log. The root mean squares have also been calculated. Where "short lives" are distinct (those indicated by an asterisk in column 5 of Tables IV and V), averages have been calculated both including and excluding them. The results are given in column 6 of the Tables, and the average lives and average log-lives have been plotted against applied stress (nominal) in Fig.1, using a logarithmic time scale.

3.4.6. **Rex.539 and En.40C Test-pieces with other Corrodents**

3.4.6.1. "Inactive" Corrodents (b,c,f,g,h - see list in section 3.3.4.) Distilled water, tap water, ammonium carbonate, potassium dichromate and potassium chromate did not cause fracture in 6 weeks (1000 hours) at 50% and 70% NTS. Some tests were continued for 8 weeks, without fracture, so these solutions have been regarded as inactive in the present context. However they do have some effect.\(^{(p.124)}\) These tests were often terminated, after 6 to 8 weeks, either by removing the test-pieces from the rig, and determining the NTS on the tensometer, or by applying sodium chloride solution until fracture occurred.

The NTS showed a significant reduction (i.e., more than 3%) in some tests. This was not studied systematically, so only examples
FIG. 14.

STRESS-CORROSION LIFE AVERAGES for REX. 539 and EN.40C in 3% NaCl against NOMINAL STRESS
can be given. The final breaking stress is given as a percentage of the original NTS in Table VI. In the same Table, the results of stress-corrosion tests with 3% sodium chloride solution after long tests with "inactive" corrodents are also given. Taking these two types of results together for both steels, certain tentative conclusions can be drawn:

(1) The reduction of NTS and of stress-corrosion life go together.

(2) Shorter periods (e.g. 360 hours), with ammonium carbonate, lengthened subsequent stress corrosion life; a long period (1610 hours) shortened the life, and a medium period (1010 hours) gave a life within the normal range.

(3) Potassium chromate and dichromate solutions seemed to be more damaging at 70% NTS, but beneficial at 50% NTS.

3.4.6.2 Sodium Sulphate and Potassium Chloride Solutions (d and e) Both these solutions were selected for comparison with sodium chloride solution, eliminating the chloride and sodium ions respectively. The concentration of 4% gives approximately the same concentration of ions as in 3% sodium chloride.

The stress-corrosion test results are included in Table VII and in Fig. 15. Comparison shows that the lives are within the same ranges, whether sodium chloride, sodium sulphate or potassium chloride is the corrodent.

3.4.6.3 Sodium Chloride with Ammonium Carbonate, Ammonium Hydroxide, and Sodium Hydroxide (i, j, k). These corrodents are grouped
### Effect of Sustained Load, with or without Corrosion, on Subsequent Stress-Corrosion Life and Notch Tensile Strength

<table>
<thead>
<tr>
<th>Steel</th>
<th>Batch</th>
<th>Applied Stress</th>
<th>Sustained Load Test</th>
<th>&quot;Corrodoent&quot; used</th>
<th>Life in 3% NaCl, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>t.s.i.</td>
<td>% NTS</td>
<td></td>
<td>Time, hours</td>
</tr>
<tr>
<td><strong>Rex 539</strong></td>
<td>A2</td>
<td>118</td>
<td>69.3</td>
<td>f. 5% (NH₄)₂CO₃</td>
<td>1610</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>119</td>
<td>70</td>
<td>g. 5% K₂Cr₂O₇</td>
<td>1465</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>119</td>
<td>70</td>
<td>g.</td>
<td>1490</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>119</td>
<td>70</td>
<td>None</td>
<td>1348</td>
</tr>
<tr>
<td><strong>En.40C</strong></td>
<td>D2</td>
<td>79.5</td>
<td>49.7</td>
<td>f. 5% (NH₄)₂CO₃</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>78.1</td>
<td>48.8</td>
<td>f.</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>114</td>
<td>71.1</td>
<td>h.</td>
<td>1010</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>111.5</td>
<td>69.7</td>
<td>h.</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>110</td>
<td>68.8</td>
<td>h.</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>80.6</td>
<td>50.4</td>
<td>h. 5% K₂CrO₄</td>
<td>504</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>79.5</td>
<td>49.7</td>
<td>h.</td>
<td>1224</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>111</td>
<td>69.3</td>
<td>h.</td>
<td>648</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>109</td>
<td>68.3</td>
<td>h.</td>
<td>576</td>
</tr>
<tr>
<td><strong>Rex 539</strong></td>
<td>A2</td>
<td>117.5</td>
<td>69</td>
<td>f. 5% (NH₄)₂CO₃</td>
<td>1440</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>121</td>
<td>71</td>
<td>f.</td>
<td>1392</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>119</td>
<td>70</td>
<td>g. 5% K₂Cr₂O₇</td>
<td>1488</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>119</td>
<td>70</td>
<td>h. 5% K₂CrO₄</td>
<td>1032</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>120</td>
<td>70.6</td>
<td>None</td>
<td>1341</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>123</td>
<td>69.6</td>
<td>None</td>
<td>1339</td>
</tr>
<tr>
<td></td>
<td>A1</td>
<td>76</td>
<td>48.2</td>
<td>a. 3% NaCl</td>
<td>265</td>
</tr>
<tr>
<td></td>
<td>C1</td>
<td>125</td>
<td>69.0</td>
<td>a.</td>
<td>168</td>
</tr>
<tr>
<td><strong>En.40C</strong></td>
<td>D2</td>
<td>80.5</td>
<td>50.3</td>
<td>f. 5% (NH₄)₂CO₃</td>
<td>1008</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>109</td>
<td>68</td>
<td>h. 5% K₂CrO₄</td>
<td>624</td>
</tr>
</tbody>
</table>
### TABLE VII

Stress-Corrosion Tests on Rex.539 and En.40C in Other Corrodents

<table>
<thead>
<tr>
<th>Corrodent</th>
<th>Stool</th>
<th>Batch Symbol</th>
<th>Applied Stress t.s.l.</th>
<th>Life hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d) 4% Na₂SO₄</td>
<td>Rex.539</td>
<td>C2</td>
<td>124</td>
<td>70.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C2</td>
<td>123</td>
<td>69.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C1</td>
<td>126</td>
<td>69.7</td>
</tr>
<tr>
<td></td>
<td>En.40C</td>
<td>D2</td>
<td>78.0</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D2</td>
<td>77.5</td>
<td>48.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D2</td>
<td>110</td>
<td>68.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D2</td>
<td>113</td>
<td>70.4</td>
</tr>
<tr>
<td>(e) 4% KCl</td>
<td>Rex.539</td>
<td>A2</td>
<td>84.5</td>
<td>49.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A2</td>
<td>86.2</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A2</td>
<td>118</td>
<td>69.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A2</td>
<td>116</td>
<td>68.3</td>
</tr>
<tr>
<td></td>
<td>En.40C</td>
<td>D2</td>
<td>78.8</td>
<td>49.2</td>
</tr>
<tr>
<td>(i) 3% NaCl + 5% (NH₄)₂CO₃</td>
<td>Rex.539</td>
<td>A2</td>
<td>83.7</td>
<td>49.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C1</td>
<td>127.5</td>
<td>70.3</td>
</tr>
<tr>
<td>(j) 3% NaCl + NH₃</td>
<td>En.40C</td>
<td>D2</td>
<td>80.0</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D2</td>
<td>76.5</td>
<td>47.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D2</td>
<td>111.5</td>
<td>69.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D2</td>
<td>112</td>
<td>70.1</td>
</tr>
<tr>
<td>(k) 3% NaCl + NaOH</td>
<td>Rex.539</td>
<td>A2</td>
<td>86.0</td>
<td>50.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A2</td>
<td>119</td>
<td>70.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A2</td>
<td>121</td>
<td>71.1</td>
</tr>
<tr>
<td></td>
<td>En.40C</td>
<td>D2</td>
<td>112</td>
<td>70.0</td>
</tr>
</tbody>
</table>
FIG. 15

Stress-Corrosion Life

Uncoated Test-Pieces in various Corrodents

REX. 539

EN. 40C

Batch:
C1/2 - A2 - A2 C2 - A2 - D2 -

% NTS:
70 50 70 50 70 50

Corrodent:
Na₂SO₄ KCI NaCl + (NH₄)₂CO₃ NaCl + NaOH
Na₂SO₄ KCl NaCl + NH₃ NaOH

LIFE - hours

S-C
together as representing sodium chloride solution with a slightly raised pH. The evaporation of ammonia from the first two solutions must result in a change of pH towards neutral soon after application to the test-piece.

The results are given in Table VII and in Fig. 15. Comparison of the relevant parts of Figs. 15, 10 and 11, especially if batch numbers are taken into account, show that lives in corrodents i, j and k are, on the whole, considerably longer than the average in 3% sodium chloride, being in the upper part of the range for sodium chloride, or slightly longer. The effect is relatively less marked for tests at 50% NTS than at 70% NTS.

The number of tests in this section is too small for firm conclusions to be drawn, so the above observations are only indicative of trends.

3.4.6.4. Sodium Chloride/Potassium Chromate Mixtures (l, m, n, o)

The object of these tests was to determine whether a passivating ion (e.g. chromate) affects stress-corrosion life. The results are given in Table VIII and Fig. 16. Only one batch of Rex.539 test-pieces was involved, and the tests were at 70% NTS. A few tests were made on En.40C.

Considering Rex.539, comparison can be made between Fig. 16 and the fifth group of Fig. 10; however a truer comparison can be obtained by abstracting the three batch C2 results from Fig. 10. These results are reproduced in Fig. 16, and also at the end of Table VIII.

A number of tests were made using a cotton-wool pad soaked in
### Table VIII

**Stress-Corrosion Tests on Rox.539 and En.40C in Sodium Chloride and Potassium Chromate Mixtures**

<table>
<thead>
<tr>
<th>Corrodent</th>
<th>Applied Stress</th>
<th>Life averages - hours</th>
<th>Life (avg of short lives)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t.s.i.</td>
<td>%NTS</td>
<td>hours</td>
<td>Ar. mean</td>
</tr>
</tbody>
</table>

**Rox.539, batch C2**

|            |               |                      |                           |           |     |
|------------|---------------|----------------------|---------------------------|-----------|
| (1) 3% NaCl + <br> 2½% K₂CrO₄ | 125.5          | 71.0                 | 1.25*                     | 10        | 4.3 |
|            | 123.5          | 69.7                 | 1.8 *p                    |           |     |
|            | 126            | 71.2                 | 3.05                      | *15       | *8.8| 22  |
|            | 124            | 70.1                 | 5.8 p                     |           |     |
|            | 123.5          | 69.7                 | 38 p                      |           |     |
| (m) 3% NaCl + <br> 5% K₂CrO₄ | 124            | 70.0                 | 12 p                      |           |     |
|            | 124            | 70.1                 | 14 p                      |           |     |
|            | 124            | 70.0                 | 362                       | 202       | 71  | 265 |
|            | 124            | 70.1                 | 420                       |           |     |
| (n) 3% NaCl + <br> 10% K₂CrO₄ | 124            | 70.1                 | 1.8 *                     |           |     |
|            | 123.5          | 69.7                 | 17 p                      | 123       | 49  | 172 |
|            | 123.5          | 69.9                 | 55 p                      |           |     |
|            | 123.5          | 69.7                 | 123 p                     | *147      | *95 | *188 |
|            | 123.5          | 69.0                 | 190                       |           |     |
|            | 125            | 70.8                 | 350                       |           |     |
| (o) 1½% NaCl + <br> 5% K₂CrO₄ | 123.5          | 69.9                 | 1.75*                     | 74        | 17  | 119 |
|            | 124            | 70.0                 | 14.5                      |           |     |
|            | 122            | 68.9                 | 206                       | *110      | *55 | *146 |
| (a) 3% NaCl | 124.5          | 70.2                 | 0.35 *p                   | 17        | 5.4 | 23  |
|            | 124.5          | 70.2                 | 11.5 p                    |           |     |
|            | 122            | 69.0                 | 39                        | *25       | *21 | 29  |

**En.40C, batch D2**

|            |               |                      |                           |           |     |
|------------|---------------|----------------------|---------------------------|-----------|
| (m) 3% NaCl + <br> 5% K₂CrO₄ | 79.7          | 49.0                 | 265                       |           |     |
|            | 79.9          | 49.3                 | 540                       |           |     |
|            | 111.5         | 69.7                 | 2.75                      |           |     |
|            | 112.5         | 70.3                 | 16                        |           |     |

**Note:** p in fourth column indicates corrodent applied by means of a cottonwool pad.
FIG. 16

Stress-Corrosion Life

Uncoated Test-Pieces in NaCl/K₂CrO₄

REX. 539 \text{ BATCH C2}

70\% \text{ NTS}

EN.40C \text{ D2}

50 \text{ AND 70\%}

NaCl \% 3 3 3 1.5 3 3 3

K₂CrO₄ \% 2.5 5 10 5 - 5 5

LOG AVERAGE

LOG AV. excl short lives
corrodent (see section 3.3.3.1). These are indicated by a "p" in column 5 of Table VIII.

Although only small numbers of test-pieces were used, certain trends are fairly clear. Corrodent 1, with only 2.5% potassium chromate, behaved much as 3% sodium chloride as regards pattern of results, with the average life shorter. Tests with corrodents m, n and o, with greater concentration of potassium chromate, showed considerably longer lives. Hence it may be concluded that potassium chromate has an inhibiting effect when in sufficient concentration; possibly it may accelerate fracture if present in insufficient amount.

Ens 40C was only tested in corrodent m. At 50% NTS, lives were unusually long, but at 70% NTS, lives were in the same range as in 3% sodium chloride.

3.4.7. Stress-Corrosion Tests on Plain Test-Pieces Unnotched test-pieces were submitted to stress-corrosion, loaded in a rig to just above and below the yield point (limit of proportionality) and sprayed with sodium chloride solution. After long periods, 4 to 8 weeks, failures occurred at the heads, where corrodent had seeped through the protective lacquer.

3.5. Preparation of Cadmium-Coated Test-Pieces

3.5.1. General Remarks. Since cadmium is commonly used to protect high strength steels in aircraft, the stress-corrosion properties of cadmium-plated steels (in addition to the hydrogen-embrittlement effects arising from the plating process) are of importance. Cadmium-coated
test-pieces were included in the investigation for this reason, and also because the effect of cadmium on the stress-corrosion of the steel might be indicative of the mechanisms occurring.

Cadmium coatings have the main function of providing a barrier to delay corrosion, and hence stress-corrosion, of the steel. Secondly, since cadmium is anodic to steel in saline solutions, the steel receives a mild cathodic protection at defects in the coating. The anodic corrosion reaction then occurs on the cadmium, and the cathodic reaction on the exposed steel. Thus the steel is protected from corrosion, but the intensified cathodic reaction might result in an increased hydrogen absorption by the steel. If the stress-corrosion mechanism involves hydrogen absorption, stress-corrosion might actually be accelerated.

Cadmium was applied by electroplating and by vacuum evaporation, after final machining. Vacuum deposition of cadmium has been suggested and developed as an alternative to electrodeposition, no hydrogen embrittlement being possible, but thicker coatings than used in the present work would be required. Thin coatings might offer a barrier to hydrogen during subsequent electroplating.

3.5.2 Cadmium Electroplating Procedure. An industrial plating bath, based on cyanides, was used, the procedure being one approved by A.I.D. for plating high tensile steels. Details are given in the Appendix.

The test-piece heads were “stopped off” with a cellulose lacquer,
so that only the central half-inch was plated. Thus the fit of the test-pieces in the chucks was unaffected. Electrical connection to the test-pieces was by copper wire wrapped round near one head before "stopping off". After plating, the lacquer was stripped. The diameters of notch and shank were remeasured (as section 3.1.4). Plating thicknesses so determined are indicated in Tables X to XII (Some recent comments on plating in notches have been made by Hartgroves and Langstone (154)).

3.5.3. De-Embrittlement and Delayed Failure Tests. The de-embrittlement treatment forming part of the plating procedure was not adequate, except for Rex.539 heat-treated to an UTS of 109 t.s.i.; at UTS 113 t.s.i., cadmium-plated test-pieces did fail under sustained load conditions.

A series of de-embrittlement tests was made on cadmium-plated test-pieces, baking at 200°C being found convenient. At this temperature, the tensile properties of both steels were not significantly affected (see section 3.1.6). A thermostatically controlled air oven was used.

Sustained load test-results are given overleaf in Table IX, for Cadmium-plated Rex.539 at UTS 118 t.s.i. and En.40C at UTS 123 t.s.i. Plain tensile test-pieces showed no embrittlement when tested on the tensometer.
Table IX. De-embrittlement Tests

<table>
<thead>
<tr>
<th>Test-piece condition</th>
<th>Sustained Load</th>
<th>Time to fail, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rex.539</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As plated</td>
<td>50% NTS</td>
<td>0.2, 0.5</td>
</tr>
<tr>
<td>Baked, 2½ hrs., 200°C</td>
<td></td>
<td>0.2, 0.8, 42</td>
</tr>
<tr>
<td>Baked, 2½+10 hrs., 200°C</td>
<td></td>
<td>25, 216</td>
</tr>
<tr>
<td>Baked, 2½+20 hrs., 200°C</td>
<td></td>
<td>&gt;240, &gt;1000</td>
</tr>
<tr>
<td>Baked, 20 hrs., 200°C</td>
<td></td>
<td>&gt;168, &gt;696, &gt;840</td>
</tr>
<tr>
<td>Baked, 18 hrs., 204°C</td>
<td>70% NTS</td>
<td>&gt;1000, &gt;1048</td>
</tr>
<tr>
<td><strong>En40C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As plated</td>
<td>50% NTS</td>
<td>0.3</td>
</tr>
<tr>
<td>Baked, 20 hrs., 197°C</td>
<td></td>
<td>&gt;168</td>
</tr>
<tr>
<td></td>
<td>70% NTS</td>
<td>&gt;888, &gt;1080</td>
</tr>
</tbody>
</table>

A 20 hour baking treatment at 200°C ± 5°C was adopted as standard.

Control tests made in the course of the stress-corrosion work showed that this was still adequate for test-pieces of higher UTS.

3.5.4. Effect of Ageing at Room Temperature Ageing at room temperature did not appear to reduce embrittlement. For example, Rex.539 test-pieces (UTS 127 t.s.i.), cadmium-plated but not baked were loaded at 70% NTS 3 and 27 days after plating; they failed after 30 and 41 minutes respectively. Records of dates of plating, baking and testing were kept, but no evidence of an ageing effect emerged.

3.5.5. Vacuum Coating Procedure The equipment consisted of a laboratory vacuum chamber in the form of a horizontal water cooled...
metal cylinder, about 15" in diameter and 24" long, with a circular
door forming one end. A rotating chuck was fitted to the closed end of
the chamber and this carried the test-piece, or several test-pieces
joined head-to-head by means of Sellotape. Thus while the coating was
being applied, the test-pieces were rotated about their axes, and were
directly over the source of evaporating cadmium. The latter consisted
of granulated cadmium metal (B.D.H. laboratory grade) in a molybdenum
foil boat, which was heated electrically. The vacuum chamber has
been briefly described by Lockington and Toth (251).

The test-pieces were degreased in acetone prior to fitting in
the chamber, and further cleaned by means of a high voltage discharge
while the chamber was being pumped down. The discharge was expected to
improve adherence of the cadmium deposit. High vacuum (about 10^-4 mm.
Hg) was obtained by means of an oil vapour diffusion pump, and the cadmium
heated until it had evaporated from the boat.

These coatings were found to be non-embrittling.

3.5.4. Replating Tests Cadmium coatings are reported to be
impermeable to hydrogen, so that such a coating could act as a barrier
to hydrogen during subsequent electroplating (139). Both de-embrittled
cadmium-electroplated test-pieces and cadmium-vacuum-coated test pieces
were further electroplated. Some embrittlement occurred (Rex.539
failed in 10 hours at 50% NTS; compare section 3.5.3.), removable by
baking. Some vacuum-coated test-pieces on which the coating blistered
during electroplating were not embrittled.
3.6. Results of Stress-Corrosion Tests (Cadmium-Coated Test-Pieces)

3.6.1. Rex.539 Test-Pieces (3% Sodium Chloride Solution) The results are given in Table X and Fig.17. Average lives have been calculated as for the uncoated test-pieces. Coating thicknesses are indicated in the Table, the figures being the average of individual determinations for the batch.

If comparison is made between the results for cadmium-coated and uncoated test-pieces of equivalent tensile properties, attention being paid to coating thicknesses, several points of interest arise:

(1) **Batch A1** test-pieces, loaded at 50% NTS Two coating thicknesses are included. The average life of test-pieces with the thinner coating is close to that for uncoated test-pieces. The thicker coatings gave an increased average life, and hence the average life for all test-pieces was rather greater than for uncoated test-pieces.

(2) **Batch C1** test-pieces, loaded at 50% NTS The coatings were of the thicker type, with a vacuum-deposited undercoat. The test-pieces did not fracture within the length of the tests; there was evidence of a slight reduction of final NTS.

(3) **Batch A2** test-pieces, loaded at 70% NTS There were only two uncoated test-pieces in this category, but if the lives of these are accepted as typical, then the thin cadmium coatings (electrodeposited or vacuum deposited) have increased the average life; the double coatings increased the life further.

(4) **Batch C** test-pieces, loaded at 70% NTS The coatings were of the
thicker type (as (2) above). The average life of these test-pieces was about three times the average life of the equivalent uncoated test-pieces (Table IV) and in particular, there were no very short lives. The test-piece without a vacuum-deposited undercoat had a life in the same range as the others.

3.6.2. En.40C Test-Pieces (3% Sodium Chloride Solution) The cadmium coatings were of two thicknesses, both classified as thin. The thinner ones were presumed liable to be imperfect, especially at the notch root where the plating thickness was estimated to be 0.0001".

The results of the tests are given in Table XI and Fig.18, and may be compared with the corresponding results for uncoated test-pieces (Table V and Fig.11). Note that:

(1) At 50% NTS, a greater proportion of coated test-pieces had very short lives.

(2) The very short lives for coated test-pieces were shorter than for uncoated test-pieces, at 50% NTS; the two longer lives exceeded the average for uncoated test-pieces.

(3) At 70% NTS, the coated test-pieces showed no very short lives and all lives exceeded the longest life for uncoated test-pieces.
TABLE X. Stress-Corrosion Tests on Cadmium-Coated Rex.539 in 3% Sodium Chloride Solution

<table>
<thead>
<tr>
<th>Batch code</th>
<th>Coat code</th>
<th>Applied Stress (t/s/i)</th>
<th>Life hours (%TS) (indicates exclusion of short lives)</th>
<th>T'mtr. test</th>
<th>Life averages - hours (Ar.mean</th>
<th>Log ave.</th>
<th>RMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>E3</td>
<td>78.5</td>
<td>50.4</td>
<td>E3 only</td>
<td>243 63 350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>E1</td>
<td>82.7</td>
<td>52.7</td>
<td></td>
<td>243 63 350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>E3</td>
<td>78.2</td>
<td>49.8</td>
<td>F1 only</td>
<td>304 189 391</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>E3</td>
<td>77.5</td>
<td>50.8</td>
<td></td>
<td>366 132 500</td>
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</tr>
<tr>
<td>A1</td>
<td>E3</td>
<td>80.5</td>
<td>51.2</td>
<td>F1 + E3</td>
<td>298 99 422</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>E1</td>
<td>79.4</td>
<td>50.7</td>
<td></td>
<td>338 158 448</td>
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</tr>
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<td>E3</td>
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<td>50.3</td>
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<td>298 99 422</td>
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<td></td>
<td>298 99 422</td>
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<tr>
<td>A1</td>
<td>V+E1</td>
<td>89.2</td>
<td>49.2</td>
<td>744</td>
<td>94</td>
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</tr>
<tr>
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<td>V+E1</td>
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<td>49.7</td>
<td>744</td>
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<td></td>
<td></td>
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<td>V</td>
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<td>V</td>
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<td>1176</td>
<td>91</td>
<td>300</td>
<td>294</td>
</tr>
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<td>677</td>
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<td>C2</td>
<td>125.5</td>
<td>70.9</td>
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<td>C1</td>
<td>126</td>
<td>69.4</td>
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<td>70.9</td>
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<td>C2</td>
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</tr>
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</tr>
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<td>360</td>
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<td>126</td>
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<td>420</td>
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<td>(720)</td>
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<td>C2</td>
<td>129</td>
<td>71.4</td>
<td>792</td>
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</tr>
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</table>

**NOTES: See foot of table XI.**
TABLE XI

<table>
<thead>
<tr>
<th>Batch Symbol</th>
<th>Coating Code**</th>
<th>Applied Stress t.s.i.</th>
<th>Life % NTS</th>
<th>Life AVERAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>E6</td>
<td>02.2</td>
<td>49.5</td>
<td>0.05</td>
</tr>
<tr>
<td>D1</td>
<td>E4</td>
<td>02.5</td>
<td>49.7</td>
<td>0.05</td>
</tr>
<tr>
<td>D1</td>
<td>E6</td>
<td>03.0</td>
<td>50.0</td>
<td>0.08</td>
</tr>
<tr>
<td>D1</td>
<td>E6</td>
<td>03.0</td>
<td>50.0</td>
<td>0.13</td>
</tr>
<tr>
<td>D1</td>
<td>E4</td>
<td>01.8</td>
<td>49.3</td>
<td>51</td>
</tr>
<tr>
<td>D2</td>
<td>E4</td>
<td>00.6</td>
<td>50.4</td>
<td>297</td>
</tr>
<tr>
<td>D2</td>
<td>E4</td>
<td>112</td>
<td>70.0</td>
<td>22</td>
</tr>
<tr>
<td>D1</td>
<td>E4</td>
<td>114</td>
<td>68.7</td>
<td>149</td>
</tr>
<tr>
<td>D1</td>
<td>E6</td>
<td>110</td>
<td>66.3</td>
<td>220</td>
</tr>
<tr>
<td>D2</td>
<td>E4</td>
<td>112</td>
<td>70.0</td>
<td>313</td>
</tr>
<tr>
<td>D1</td>
<td>E6</td>
<td>116</td>
<td>69.8</td>
<td>408</td>
</tr>
</tbody>
</table>

** NOTES TO TABLES X and XI

Coating Code:

V = cadmium vacuum-coating, 0.0002" to 0.00035"
E1 = cadmium electroplating, 0.002" to 0.0025", 0.00075" in notch
E2 = " 0.0015" 0.001" in notch
E3 = " 0.0009", 0.0003" in notch
E4 = " 0.00075", 0.0004" in notch
E5 = " 0.0005", 0.0002" in notch
E6 = " 0.0003", 0.0001" in notch

Life: Results for test-pieces which did not fail are shown in brackets. In calculating average life, these figures have been increased slightly, e.g. (672) to 700, (1176) to 1200, and (720) to 750.
FIG. 17

Stress-Corrosion Life

CADMIUM COATED REX.539 in 3% NaCl Solution

Batch:
Coating: E = Electroplated, V = Vacuum coated
% NTS: 50 - 70
FIG. 18
Stress-Corrosion Life
CADMIUM-PLATED EN.40C
in 3% NaCl Solution
3.6.3. Corrodents other than Sodium Chloride

The results of the few tests made are given in Table XII. Additional notes follow:

**Corrodent (d), 4% sodium sulphate**  The lives tended to be longer than in the corresponding tests with sodium chloride (Tables X and XI).

Rex 539 at 70% NTS and En 40C at 50% NTS did not fracture in 8 weeks, and, judging from the normal life on subsequent application of sodium chloride solution, the sodium sulphate had done no damage. However, En 40C loaded at 70% NTS and above was sensitive to the corrodent; the lives were slightly longer than when sodium chloride was used.

**Corrodent (f), 5% ammonium carbonate**  No fracture occurred in over 9 weeks at 70% NTS (1 test), confirming previous observations with uncoated test-pieces. Life after application of sodium chloride was of normal length.

**Corrodent (h), 5% potassium chromate**  Two tests were made, for 9 and 11 weeks respectively, at 70% NTS. As no fracture occurred, corrodent (m), (3% NaCl/5% K₂CrO₄) was applied for a period, followed by sodium chloride solution, as indicated in the last column of the Table.

Although the test-pieces were rinsed before applying sodium chloride solution, the yellow chromate was leached out for about three weeks. One test-piece broke when distilled water was dripped on to the notch for four hours in a final attempt to remove all traces of chromate. The other test-piece did not break even after the cadmium had been scraped from the notch root and sodium chloride re-applied; chromate was still
### TABLE XII

**Stress-Corrosion Tests on Cadmium-Plated Rev.53g and En.40C in Solutions Other than Sodium Chloride**

<table>
<thead>
<tr>
<th>Corroden</th>
<th>Batch Symbol</th>
<th>Coating Code**</th>
<th>Applied Stress t.s.i.</th>
<th>%NTS Life hrs***</th>
<th>Further Tests (notes, **)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d) 4% $\text{Na}_2\text{SO}_4$</td>
<td>A2</td>
<td>E5</td>
<td>119</td>
<td>70.0 (1320)</td>
<td>3% NaCl (528 hr) T. 97% NTS</td>
</tr>
<tr>
<td>D2</td>
<td>E4</td>
<td>80.5</td>
<td>50.3 (1488)</td>
<td>3% NaCl, 489 hr.</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>E4</td>
<td>111.5</td>
<td>69.8</td>
<td>409</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>E4</td>
<td>120.5</td>
<td>75.4</td>
<td>168</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>E4</td>
<td>130</td>
<td>81.3</td>
<td>110</td>
<td></td>
</tr>
</tbody>
</table>

| (f) 5% $(\text{NH}_4)\text{CO}_3$ | D1 | E4 | 116 | 70.0 (1584) | 3% NaCl, 204 hr. |

| (h) 5% $\text{K}_2\text{CrO}_4$ | A2 | E5 | 119 | 70.0 (1518) | 3% NaCl + 5%$\text{K}_2\text{CrO}_4$, (576 hr); 3% NaCl, (552 hr.) Fractured when thoroughly rinsed. |
| A2 | E5 | 119 | 70.0 (1944) | 3% NaCl + 5%$\text{K}_2\text{CrO}_4$, (1176 hr.) 3% NaCl, (2856 hr.) Scraped, 3% NaCl, (192 hr.) T. 89% NTS |

**NOTES:** Coating code: See footnotes to Table IX

Life: Results for test-pieces which did not fail are shown in brackets.

Further tests: As last note; T. = tensometer test.
colouring the corrodon. In this test, the final NTS was found to be 11% below standard.

3.7 Additional Observations

3.7.1. Effect of Ambient Conditions (see section 3.3.3.2.) Owing to the large variation in stress-corrosion lives, it was not possible to correlate time of failure with day-to-day conditions. It was hoped to show that seasonal conditions had an effect (e.g. periods of hot weather, high humidity, etc.), but a survey of the results showed that any such effect must be small compared with the variation in life. Laboratory fumes (acid fumes, hydrogen sulphide, etc.), entering the testing room in small amounts, appeared to have no effect.

3.7.2. Time Interval between "Spraying" and "Fracture" Records of time of last application of corrodonent and time of fracture showed no preferred interval. Intervals ranged from a few minutes to nearly 24 hours. Longer intervals may have occurred at weekends when the timing device was not fitted.

3.7.3. Corrosion Observations Qualitative notes were taken of the progress of corrosion, as indicated by the corrosion products, during the course of the stress-corrosion tests. This topic was not studied in a fully systematic way, but a number of general observations were made.

(1) Stress-corrosion failure did not depend on total corrosion, nor even on the quantity of product visible in the notch. Fractures did occur before any corrosion products were observed; conversely, some test-pieces were completely covered with rust without fracture.
(2) Obviously, test-pieces which do not break will show eventually more total corrosion. However on several occasions, when duplicate tests were run together, the test-piece on which general corrosion developed more rapidly had the longer life.

(3) Point corrosion at the notch-root (and elsewhere on the test-piece) was often observed, and presumed to indicate pitting.

(4) With cadmium-coated test-pieces, the cadmium corroded initially, the products being white. Frequently it was noted that fracture occurred shortly after iron corrosion products first appeared.

3.7.4 Visual Examination of Fracture Surfaces The broken test-pieces were examined as soon as possible, and the features of the fracture surface, as seen by eye and with a lens, noted. Several fracture types could be distinguished, and the typical features are described below. The descriptions refer to one half of the test-piece, viewed with the fracture surface uppermost; features described as "above level of notch-root" correspond to features "below level of notch-root" on the other half of the test-piece. Diagrammatic plan views of typical fracture surfaces are given in Fig. 19, which, with the diagrams of typical fracture profiles of Fig. 20, will make the descriptions clearer.

(a) Test-pieces broken on the tensometer, for NTS determination or after a sustained load or stress-corrosion test, had fairly flat fracture surfaces, level with the notch-root. A slight cleavage effect sometimes raised part of the circumference above the centre of
the notch-root, but not above the radiused part of the notch.

(b) Test-pieces embrittled during electroplating often showed bright, very smooth areas near the notch root after "delayed failure". These cleavage surfaces were at about 45° to the plane of the notch, sometimes forming a series of "teeth" and "notches" round the circumference of the fracture. They usually met the notch surface beyond the radiused root. A baking treatment, even if inadequate to prevent delayed failure, eliminated the bright surfaces.

(c) One typical stress-corrosion fracture surface was slightly oblique, with a ridge extending part of the way round the circumference, the fracture meeting the surface above the notch-root; the rest of the circumference was depressed below the level of the notch-root. Where the fracture surface met the notch root, a small darker or duller area could often be distinguished. A corresponding area was present on the other half of the test-piece.

(d) In another typical form, the fracture surface was level with the notch root on one side, where there was a darker area. The surface was then directed obliquely downwards towards the opposite side, finally rising steeply to above the level of the notch-root. Again, there was a corresponding darker area on the other half of the test-piece (See Fig.21).

(e) Less commonly, the stress-corrosion fracture surface was flat, below the level of the notch root, the circumference being raised to the notch root, or just above it, as a ridge.
b. Delayed failure hydrogen embrittlement

c. Indistinct Primary Fracture

d. Primary Fracture

e. Indistinct Primary Fracture

FIG. 19.
Sketches of Plan Views of Fractured Surfaces.
(see section 3.7.4.)
FIG. 20. Diagrams of Typical Axial Sections through the Fractures of Notched Test-pieces. (see section 3.7.4.)
Fig. 21 (A and B) Fractured test-piece viewed from two angles. (x = primary fracture).
The "darker areas" were most clear when a sodium chloride/potassium chromate corroden was used. The appearance suggested a difference in reflectivity or grain pattern rather than a stain due to corrosion product. With sodium chloride corroden, sufficient corrosion product was often formed to discolour the area, and mask to some extent the limits. At least a part of the corrosion product was formed after fracture, since although the areas corresponded in position on each half of the test-piece, the amount of product was sometimes greater on one half. The amount of corrosion product on the fracture surface would clearly be affected by the amount of unevaporated water at the time of fracture, by how much corroden splashed on to the fracture surface, and by the time interval between fracture and rinsing. If this interval was very short, the fracture surface seemed free of product.

The darker areas were assumed to be due to the inward spread of a stress-corrosion crack, and to be differentiated from the remainder of the fracture surface (due to mechanical failure only) by the different crack path or propagation mechanism and by the possibility of corrosion. These areas always intersected the test-piece surface on the radiused part of the notch-root, and sometimes there was a spot of rust on the notch surface at this intersection, the rust not extending on to the fracture surface. Such point corrosion often did not quite coincide with the fracture/surface intersection.
The position of the darker area (clearly the primary fracture of Hughes et al. \textsuperscript{(223)}) was independent of the orientation of the test-piece heads before mounting in the rig, as described in section 3.3.2. Only once were two darker areas found, and these were contiguous.

3.7.5. Metallographic Examination Axial sections of fractured test-pieces were made by grinding a flat on the cylindrical shank surface parallel to the intended section, (the head being cut off, or ground down to the same level), mounting in bakelite and grinding down mount and test-piece, parallel to the flat, until the axis was reached. The width of the section should then be equal to the diameter of the test-piece.

While grinding down, examination was made for visible cracks near the notch, and occasionally the surface was given an adequate polish for microscopic examination. No additional cracks were observed.

The axial sections were polished to a good metallographic finish, and examined under the microscope as polished and as etched with 2\% nital. Figs. 22 to 25 are typical photomicrographs, illustrating structure and fracture. Fractures were intergranular.

Most sections were made through the primary fracture area. Both halves of test-pieces were sectioned, in order that any branching of the stress-corrosion crack would be observed. Only one branch crack was found, and this is just visible in Fig. 22. A few test-pieces which had been removed from the sustained load rig before failure were also sectioned, but no cracks found.
Fig. 22  Typical section through fracture, Rex. 539.  x 100; etchant: nital.

Fig. 24  Structure of Rex.539. x 405; etchant: nital. (2 specimens).

Fig. 23  Fracture and steel structure, Rex.539. x 405; etchant: nital. (Shows only subsidiary crack observed).

Fig. 25  Structure of En.40C. x 625; etchant: nital.
Confirmation of cadmium-plating thicknesses was also obtained.

3.7.6. **Fracture Profiles** Test-pieces were placed vertically on the microscope stage, fracture uppermost, and the fracture surface "contours" plotted, using the stage micrometer movement, and calibrated fine focussing. The only point of note was that there was a change in general direction of fracture at the limits of the primary fracture area. Unless this area was definitely corroded, it was far less obvious under the microscope than when examined with a simple lens. Plots of fracture profiles were also made from the axial sections of test-pieces, using the stage micrometer movement and an eyepiece grid. Typical profiles have already been illustrated, Fig.20. The angle between the general direction of the primary fracture and the plane of notch-root was usually in the range 20° to 30°.

3.8. **Additional Experiments.**

3.8.1. **Cathodic Charging Tests** The test-piece was mounted in the rig, the load being pre-set but not applied to the test-piece. Cotton-wool was wrapped round the test-piece, and bound in place with platinum wire, the wire not contacting the test-piece. A 3-volt battery was then connected across the wire and test-piece (the latter being made cathodic) and the cotton-wool then wet with 4% v/v sulphuric acid. Laboratory reagent grade acid was used, without the addition of "poisons". A current of about 1 ampere was passed, for 5 to 30 minutes. The cotton-wool was then removed, the test-piece
rinsed with distilled water and alcohol and dried with filter paper.

The load was applied to the test-piece after an interval of 1 to 70 minutes.

Tests were also made in which the test-piece was cathodically charged while under load.

The results, in brief, were as follows:

(1) Longer charging times produced more rapid failures after loading.

(2) Longer intervals between charging and loading increased time to fail after loading - this seemed the most important factor.

(3) Charging while loaded produced immediate or very rapid failure.

(4) A sustained load applied for a period before charging (load removed for charging) decreased time to fail.

The results in Table XIII illustrate these observations.

**TABLE XIII**

Cathodic Charging Tests on Rex 539

<table>
<thead>
<tr>
<th>Time on load before charging</th>
<th>Charging time</th>
<th>Interval before (re-)loading</th>
<th>Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Rex. 539, UTS 113 t.s.i., NTS 158 t.s.i.; stress 62% NTS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 days</td>
<td>5 minutes</td>
<td>70 minutes</td>
<td>68 hours.</td>
</tr>
<tr>
<td>10 days</td>
<td>10 minutes</td>
<td>60 minutes</td>
<td>63 hours.</td>
</tr>
<tr>
<td></td>
<td>10 minutes</td>
<td>30 minutes</td>
<td>6 hours.</td>
</tr>
<tr>
<td></td>
<td>10 minutes</td>
<td>30 minutes</td>
<td>2 minutes.</td>
</tr>
<tr>
<td></td>
<td>10 minutes</td>
<td>60 minutes</td>
<td>0 hours.</td>
</tr>
<tr>
<td>(b) Rex. 539, batch C2; applied stress 70% NTS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14 days</td>
<td>5 minutes</td>
<td>20 minutes</td>
<td>2 1/2 hours</td>
</tr>
<tr>
<td>15 days</td>
<td>15 minutes</td>
<td>20 minutes</td>
<td>0 hours.</td>
</tr>
<tr>
<td>14 days</td>
<td>5 minutes</td>
<td>20 minutes</td>
<td>18 minutes</td>
</tr>
</tbody>
</table>
The fractures of freshly charged test-pieces took the form (b) of section 3.7.4, but after ageing fractures tended to be of forms (d) and (e), without "darker areas". Test-pieces which had a short charging treatment (5 minutes) had fractures nearer form (c).

3.8.2. Stress-Corrosion Tests on Silicone-Coated Test-Pieces.

Rex.539 test-pieces, batch Cl, were dipped in a hard silicone stoving lacquer (Corrux Silicone H.R., Finish Clear, 5.H.5388), allowed to drain for a short time, and stoved at 200°C for 2 hours in air. Sufficient lacquer was removed from the heads to allow a correct fit into the chucks.

The test-pieces were loaded at 50, 70 and 80% NTS, and the stress-corrosion test started after the usual preliminary 7 days on load. If no failure occurred in 3 to 4 weeks, the lacquer was scraped from the notch-root using a needle, and the test continued. In one test, the notch root was scraped at the start. The stress-corrosion lives were as Table XIV.

The lacquer did not prevent corrodent reaching the steel surface completely, patches of rust being noticeable after several weeks. However, in the notch, where the lacquer was thicker, only a light rust colour was developed in the lacquer and evidently permeation of corrodent here was insufficient to cause stress-corrosion at 50% and 70% NTS, but sufficient to cause quite rapid
failure at 80% NTS. The lacquer did not show any cracks.

**TABLE XIV**

**Stress-corrosion Tests on Silicone-Lacquered Test-pieces - Rex. 539, batch Cl.**

<table>
<thead>
<tr>
<th>Applied stress</th>
<th>Time on test before lacquer scraped from notch</th>
<th>Life after lacquer scraped from notch</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% NTS</td>
<td>4 weeks</td>
<td>29, 80* hours</td>
<td>2 tests</td>
</tr>
<tr>
<td>70% NTS</td>
<td>4 weeks</td>
<td>1 1/2*, 22, 74 hrs.</td>
<td>3 tests</td>
</tr>
<tr>
<td></td>
<td>3 weeks</td>
<td>171 hours</td>
<td>notch scraped at start.</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>48 hours</td>
<td></td>
</tr>
<tr>
<td>80% NTS</td>
<td>1 1/2, 120, 258 hrs.</td>
<td>---</td>
<td>failed before notch scraped.</td>
</tr>
</tbody>
</table>

* These test-pieces were removed from the rig for scraping, re-loaded, and corrodent applied again 1 hour later.

Earlier tests at 75% NTS (with batch B test-pieces) had shown that no failure occurred in 9 weeks without corrodent; with 3% sodium chloride applied, one test-piece failed in about a week, the other not failing in 7 weeks. At this stress, it appears that the lacquer may or may not prevent stress-corrosion.

Comparison with Fig. 10 shows that at 80% NTS, failure was delayed by the lacquer. At the lower stresses, after the lacquer had been scraped from the notch, leaving clean metal beneath, the lives were in the same range as the lives of unprotected test-pieces.

The fracture surfaces had no features of special interest.
3.8.3. Potential Measurements between Cadmium and Steel Test-Pieces

Simple potential measurements were made between cadmium and Rex.539 and cadmium and En.40C, partly immersed in sodium chloride and sodium sulphate solutions, using a potentiometer, in order to have an indication of the size of galvanic effects when cadmium plated test-pieces were undergoing stress-corrosion.

A 1/8"-diameter rod of cadmium (B.D.H. - laboratory reagent grade) was used, immersed surface area being approximately 2 sq. ins. The steel samples were broken test-pieces, with clean machined surfaces, immersed surface areas being of the order of 0.2 sq. ins. The solutions were at room temperature, and were aerated before use.

The first test was made in 3% sodium chloride; the test-pieces were then transferred to 20% sodium chloride; then, after rinsing, to 4% sodium sulphate solution. The steels were positive (cathodic) relative to cadmium, the potential differences being given in Table XV.

The cadmium and steel electrodes were on open circuit, except when potential measurements were being made.

The potential difference between cadmium and steel in aerated moving sea water has been given as 0.09 volts (ref. 6 p. 231).

In 3% NaCl solution, En.40C rapidly reached a potential of -0.48 volts against S.C.E., falling in 30 minutes to -0.54 volts.
### TABLE XV

**Potentials between Cadmium and Steels.**

<table>
<thead>
<tr>
<th>(1) 3% NaCl</th>
<th>Rox 539</th>
<th>En 40C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>0.33 volts</td>
<td>0.41 volts</td>
</tr>
<tr>
<td>Falling rapidly to</td>
<td>0.217 volts</td>
<td>0.335 volts</td>
</tr>
<tr>
<td>After 20 minutes</td>
<td>0.188 volts</td>
<td>0.299 volts</td>
</tr>
<tr>
<td>After 30 minutes</td>
<td>0.179 volts</td>
<td>0.276 volts</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(2) 20% NaCl</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>0.243 volts</td>
<td>0.338 volts</td>
</tr>
<tr>
<td>After 10 minutes</td>
<td>0.226 volts</td>
<td>0.303 volts</td>
</tr>
<tr>
<td>After 15 minutes</td>
<td>0.223 volts</td>
<td>0.299 volts</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(3) 4% Na₂SO₄</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>0.110 volts</td>
<td>0.196 volts</td>
</tr>
<tr>
<td>After 5 minutes</td>
<td>0.097 volts</td>
<td>0.179 volts</td>
</tr>
<tr>
<td>After 10 minutes</td>
<td>0.097 volts</td>
<td>0.162 volts</td>
</tr>
</tbody>
</table>

### 3.9. Summary of Investigation

#### 3.9.1. Experimental Procedure

The work was concerned with the stress-corrosion behaviour of two low alloy high-tensile steels. Rox 539 was used for the majority of experiments, a sufficient number of tests being made with En 40C to show that its behaviour was similar. Both steels were heat-treated to strength levels near 120 t.s.i.

The tests took the form of daily application of corroden (e.g. 3% sodium chloride solution) to notched tensile test-pieces under sustained loads equivalent to 33, 50, 70, and 80% of the notch tensile strength (NTS), most tests being made at 50 and 70% NTS. Stress-corrosion "life", i.e. time interval between the first application
of corrodent and the fracture of the test-piece, was recorded.

Cadmium-plated test-pieces, as expected, showed "delayed failure". This effect was eliminated by baking at 200°C for 20 hours, and then the cadmium-plated (and cadmium vacuum-coated) test-pieces showed stress-corrosion behaviour similar to that of the uncoated specimens.

To avoid false results from early failure due to causes other than stress-corrosion (e.g. residual hydrogen embrittlement, accidental defects at notch) test-pieces were stressed for a week before corrodent was applied. Also, sustained load tests were made for periods well in excess of normal stress-corrosion life.

Additional tests were made with cathodically charged test-pieces, and with test-pieces coated with a silicone-based lacquer.

3.9.2 Results The comments below numbered 1 to 5 refer to stress-corrosion of uncoated Rex 539 in 3% sodium chloride solution, since this combination formed the greater part of the work. Using these results as "standard", the other results are given and compared in comments numbered 7 to 20.

**Rex 539/3% NaCl**

(1) The stress-corrosion life range for each condition of test was very wide, so that a logarithmic time scale was used in graphical presentation of results, and also for deriving a representative figure for life under each condition. This figure is referred to as "log. average life".

(2) At 33% NTS, stress-corrosion life exceeded 1344 hours (8 weeks).
(3) At 50% NTS and 70% NTS, two life ranges were apparent: very short lives of the order of 1 hour and less and normal lives in the ranges 28 to 780 hours at 50% NTS and 12 to 670 hours at 70% NTS. Hence there is a trend to shorter normal lives at the higher stress, although the ranges overlap.

(4) At 80% NTS, lives were much shorter.

(5) When strength level (UTS) is taken into account, a trend to longer life at lower UTS for a given % NTS was apparent (Fig. 10). Lower UTS implies a lower applied stress for a given % NTS, so that life and average life plotted against applied stress illustrated the same point (Figs. 12 and 14).

(6) No significant reduction in NTS was observed in test-pieces removed from the rig before failure, even after periods close to the expected life.

En. 40C/3% NaCl

(7) En. 40C showed the same characteristics as Rex.539, but was more susceptible to stress-corrosion in the sense that the lives were much shorter for equivalent conditions (UTS, %NTS). There were some very short lives of a few minutes only, but there was not such an obvious gap in life-range distinguishing "very short" and "normal" lives as with Rex.539.

(8) Two batches of En.40C test-pieces were used, of the same UTS. The noticeable difference in NTS and in susceptibility to SCC between batches further indicated the sensitivity of this material.
(9) Applied stresses were limited to 50% and 70% NTS.

**Other Corrodents**

(10) Tests in sodium sulphate and potassium chloride solutions gave lives in the same range as in sodium chloride solution.

(11) Lives in sodium chloride solution of slightly raised pH were a little longer, more noticeably so at 70% NTS than at 50% NTS.

(12) Some "corrodents" - distilled water, tap water, ammonium carbonate, potassium chromate and potassium dichromate solutions - did not cause comparable stress-corrosion.

(13) Long tests in "inactive corrodents" had some effect, in reducing NTS and subsequent life in 3% sodium chloride solution. Potassium dichromate and chromate solutions appeared to passivate at 50% NTS. (See section 3.4.6.1.)

(14) Long sustained load tests, in air, did not cause a reduction in NTS or in subsequent stress-corrosion life.

(15) Mixtures of sodium chloride and potassium chromate (in the ratios 3:2.5 to 3:10) produced stress-corrosion effects. The lowest concentration of potassium chromate accelerated stress-corrosion failure; in higher concentrations, potassium chromate had an inhibiting effect, increasing stress-corrosion life. This was most marked for En 40C at 50% NTS.

**Cadmium-coated Test-pieces**

(16) Cadmium-coated test-pieces, de-embrittled by baking, failed by stress-corrosion in a similar way to uncoated test-pieces.
(17) Normally thick cadmium coatings eliminated very short lives, and the average life was increased over that for uncoated test-pieces, even when very short lives of the latter were excluded from the average.

(18) With very thin coatings, some very short lives were observed at 50% NTS, but not at 70% NTS. These lives were shorter than those of uncoated test-pieces.

(19) Sodium sulphate was markedly less aggressive than sodium chloride (compare with (10)), excepting En.40C at 70% NTS, the lives being not much longer in sodium sulphate than in sodium chloride.

(20) Potassium chromate did not cause fracture, and appeared to have an inhibiting effect when sodium chloride solution was subsequently applied.

**Corrosion Observations.**

(21) General corrosion, as indicated by the amount of corrosion product, seemed to be unconnected with the cracking phenomenon. (There was some evidence that test-pieces which showed general corrosion more quickly had rather longer lives).

(22) Point corrosion (pitting) at the notch root often preceded failure.

(23) Iron corrosion products were noticed on cadmium-plated test pieces shortly before failure.
Fracture Observations

(24) Usually a small area of the fracture surface was differentiated, and this was assumed to be formed by a stress-corrosion mechanism.

(25) This area intersected the test-piece surface at or very near the notch-root, where there was sometimes point corrosion. Most or all of the corrosion product on the fracture surface seemed to have formed after failure.

(26) The rest of the fracture was consistent with mechanical failure of the reduced cross-section, the profile indicating development of a non-axial load as the fracture spread across the section. (See 3.7.4.)

(27) With the exception already noted, no additional cracks were found, nor was there evidence of more than one stress-corrosion area.

(28) The fractures were intergranular.

Additional Observations

(29) Corrosion before applying the load had no effect.

(30) Plain test-pieces (not notched) did not fail. (Eventual failure at the head, due to seepage of corrodent, sometimes occurred).

(31) Cathodic charging of test-pieces resulted in behaviour expected from the literature. In particular, charging a stressed test-piece gave much more rapid failure than charging before
stress was applied.

(32) Test-pieces protected by a coat of stoving lacquer did not fail by stress-corrosion at below 75% NTS. The coating delayed failure at 80% NTS. Removal of the lacquer from the notch resulted in stress-corrosion failure, the life being as for unprotected test-pieces.

(33) Cadmium was about 0.2 volts anodic to Rex.539 in sodium chloride solution, about 0.1 volt in sodium sulphate. The figures for En.40C were about 0.3 and 0.2 volts respectively.
4. DISCUSSION

4.1. Introduction

The results have been presented, with some comment on each series of tests, and the main points have been listed as a basis for discussion.

The test results themselves need little further discussion, but the characteristics of the effect under investigation will be examined with a view to establishing a mechanism. This effect can clearly be classified as stress-corrosion cracking, since fracture of the notched test-pieces resulted from the conjoint action of stress and corrosion. Neither stress alone nor corrosion alone affected the length of subsequent stress-corrosion tests, in contrast with some stress-corrosion systems where stress is reported to be unimportant during part of the induction period.

The presence of an induction period, occupying almost the whole life of the test-piece, was clearly indicated by the failure to detect a loss of strength in the course of the test, and so the mechanism must involve an induction period leading up to crack nucleation and rapid crack propagation.

The available broad mechanisms, according to the literature, are as follows, stress being necessary in each.

(1) SCC - Stress-corrosion cracking in a restricted sense, relying only on anodic processes such as pitting attack and accelerated or preferential corrosion at the crack tip to explain crack nucleation and growth.
HEC - Hydrogen embrittlement cracking, the hydrogen resulting from the cathodic corrosion reaction, and being absorbed by the steel.

SSC - Stress-sorption cracking, whereby crack propagation is made easier by the adsorption of components of the environment, especially on the freshly formed faces of the growing crack.

The distinction between "SCC" and "HEC" is a matter of convenience; when the hydrogen is absorbed as a result of corrosion during the stress-corrosion test (and especially if the hydrogen is only absorbed when stress is present), HEC falls well within the usual definitions of stress-corrosion cracking. In the following pages "SCC" will be used in the restricted sense, excluding HEC processes, and the words "stress-corrosion cracking" in the more general sense.

The operation of one of these processes does not exclude the others, and the processes operating during the induction period need not be the same as those during the period of crack propagation. For example, SCC might serve to nucleate a crack by forming a pit, and crack propagation might be accelerated by SSC. It is more difficult to understand how a crack could be nucleated by SSC.

It follows that the conditions required for crack nucleation may be unnecessary for crack propagation. Conversely, conditions which can nucleate a crack might not be adequate for propagation, although this situation would not seem likely.

4.2 Original Conclusions regarding Mechanism

The following paragraphs are taken from the final report on the
testing work (1), the wording being only slightly edited to fit the present context; the references back refer to this thesis.

"Several of the points enumerated in section 3.9.2, - lesser sensitivity of the silicon-containing Rex539, greater sensitivity at higher strength level, and the slight effect of corrosion before stressing (points 7,5,29 respectively) - indicate an analogy with hydrogen embrittlement. It is assumed that hydrogen generated by the corrosion reaction is absorbed by the steel, initiating fracture.

"Fracture brought about by cathodic charging of test-piece under stress is much more rapid than when the charging is done before applying stress. The effect of corrosion seems to be similar in this respect, and it is possible that corrosion in the absence of stress has no effect at all. With the usual corrosion mechanism, under aerated conditions, the liberation of hydrogen would not be expected, but under the special conditions at the notch of a stressed test-piece, although molecular hydrogen may not be formed, hydrogen may be absorbed by the steel. Once a crack has been initiated, the extra concentration of stress would further assist the mechanism.

"With coated test-pieces, it was thought that the relative positions of the coating metal and the steel in the galvanic series would have an effect on corrosion-induced failure. In particular, a "sacrificial" coating (e.g. zinc, cadmium) would favour a corrosion
mechanism by which hydrogen would be liberated at the steel surface, so that such a coating, if porous or defective, would create greater risk of failure. This effect could, of course, be masked by the general corrosion protection given by the coating; it is difficult to assess the relative qualities of various coatings at the notch root.

"Point (10) indicates that the chloride ion is not necessary to the corrosion-induced failure mechanism (as it appears to be with some stress-corrosion cracking phenomena). However, the chloride appears to penetrate a coating more quickly than the sulphate (point 19).

"The unpredictability of time to fail for individual test-pieces indicates that there is an element of chance involved. The time to fail may include an "induction" period of variable length, and a period during which a crack is developing. This latter period is probably short, to account for rapid failures, and less variable (than the induction period) for tests under given conditions.

"A special type of corrosion mechanism may develop in the notch. This may be called an "active corrosion point", since the evidence from the examination of fractures is that fracture starts at a point or short length at notch root. It is assumed that corrosion must be intense at the point in order to start a crack.

"The development of an active corrosion point may be brought about by:
(i) Presence of inclusions, oxide film, etc. at steel surface.
(ii) Irregularities in shape of notch root.
(iii) Presence of defects in coating, of suitable size and position.
(iv) Formation of defects due to corrosion of coating on steel surface.
(v) Formation of local corrosion cell due to differential aeration, salt concentration, distribution of corrosion products, etc.

"The accidental presence of a suitable defect, suitably placed at the notch, would cause very rapid failure of the test-piece. If no such defect is present, time will be required for the development of the necessary conditions for fracture. During this period:

(i) With uncoated test-pieces, corrosion products may change conditions, so that an "inactive" defect becomes "active".
(ii) The coating may be penetrated, by corrosion if metallic, or by other mechanism for paints or lacquers. Eventually, a suitable defect is formed or uncovered, and rapid failure follows.

The rapid process by which the active corrosion point brings about fracture cannot be defined at this stage. A strong non-oxidising electrolyte appears to be necessary. Weaker electrolytes (ammonium carbonate) and oxidising ions (chromate) do not cause
fracture.

"The reduced rate of attack of sodium sulphate on coated specimens shows that rate of penetration of the coating is an important factor.

"There is evidence, not yet conclusive, that corrosion occurring actively away from the notch inhibits fracture (point 20). Possibly a "sacrificial" coating could do the same. The effect of such "cathodic protection" could be (a) to prevent corrosion in the vicinity of the notch or (b) to promote a cathodic action, with formation of hydrogen. Hence if the cathodic protection is inadequate, (b) would preponderate, and risk of failure might be increased."

4.3. Further Discussion of Results

4.3.1. Scatter of Stress-Corrosion Lives The lack of reproducibility in time to fail gave some concern during the testing work. The scatter could not be attributed to the peculiarities of individual rigs, to visible test-piece defects, nor to variations in ambient conditions, and so it had to be assumed that the scatter was characteristic of the stress-corrosion process, and that the mechanism included some element of chance.

The unusually wide range of stress-corrosion lives for high-strength steels has been noted by others (e.g. Davis[222]), and delayed fracture tests on hydrogen embrittled high-strength steels have shown similar scatter, especially when stresses are in the intermediate range[139,141]. Possibly the high stress concentration with notched test-pieces introduces
a certain instability as well as greater sensitivity to embrittlement
and stress-corrosion, and hence increases the degree of scatter in the
results.

The use of a logarithmic time scale when displaying the results
in diagram form appears to have been fortuitous, and taking the average
log. life as representative of a set of results is justified in view of
the work of Booth et al.\(^{248,249}\). Whether any average of the smaller
sets of results has any statistical significance is another matter;
however, since the discussion and conclusions which follow do not
depend on exact values of average life under the various conditions, but
only on the clear trends shown as conditions were changed, a wide
standard deviation is acceptable. Confidence in using average values
is increased when all the results are taken together, since a reasonable
pattern is formed; in other words, when average log. life is plotted
against a variable, a reasonably smooth curve results (fig.14). If
other averages, namely the arithmetic mean, and the root mean square,
are plotted, the same general trends are apparent.

4.3.2. De-embrittlement after Cadmium Plating  No great difficulty
was experienced in de-embrittling the cadmium-plated test-pieces,
contrary to a number of reports concerning cadmium plated ultra-high
strength steels. In the present work, only the centre part of the
test-pieces was plated, so that on baking the hydrogen could be readily
dispersed to the heads of the test-pieces, and also evolved from the
uncoated surfaces, thus reducing the concentration to a sufficiently low.
In the case of very thin plating, hydrogen may have been evolved from the notch root (154,155).

4.4. Discussion of Mechanism

4.4.1. Conditions for Stress-Corrosion Failure The basic conditions under which ultra-high strength steels crack in near-neutral environments were found to be:

(1) The environment should be strongly corrosive towards the steel.

(2) A stress-concentration must be present; a notch in the experiments.

(3) The applied stress must exceed a certain value – about 35% NTS for failure within six weeks when the steel is heat-treated to a strength level of about 120 t.s.i.

These conditions differ from those applying to most stress-corrosion systems in several particulars. In addition to the points noted by Brown (218), namely the non-specific nature of the environment and room temperature operation, the aggressive nature of the environment with regard to general corrosion is of special interest.

Usually, stress-corrosion occurs more readily in environments which give very little general corrosion attack on the metal, so that selective attack at certain points, enhanced by stress, may be the more intense. General corrosion often reduces susceptibility to stress-corrosion. For example, stainless steel in insufficiently concentrated boiling magnesium chloride solution may suffer widespread pitting attack instead of cracking (253); chloride additions
to boiling nitrate solutions make nitrate cracking of carbon steels less likely (200); chromates are added to chloride solutions to minimise pitting of aluminium- and magnesium-based alloys, and thus make stress-corrosion tests more sensitive (246).

The effect of general corrosion rate on the susceptibility of the ultra-high strength steels to cracking is not clear. The addition of chromates to chloride solutions decreased stress-corrosion life for small additions, and increased life for larger additions, (Fig. 16) so that the rate of cracking changed in the same sense as the expected rate of corrosion. However point 21 of section 3.9.2. indicates the opposite. The fact that the frequency of application of corrodent made little or no difference to the total stress-corrosion life also has a bearing on this topic, suggesting that during the greater part of the life, a continuously fast corrosion rate is unnecessary and fluctuations in corrosion rate do not result in equivalent fluctuations in the rate of the controlling stress-corrosion mechanism.

4.4.2. Possible Mechanisms The stress-corrosion life consisted of an induction period followed by a period of crack propagation (see 4.1. and 4.2.). This is, of course, in keeping with suggested or established mechanisms for a number of other stress corrosion systems.

In the present tests, the period of sustained load before the corrodent was applied appeared to contribute nothing towards the eventual fracture of the test-piece, even under mildly corrosive
conditions. It follows then that the induction period (and the "life") started with the first application of an active corrodent. There was no indication of the beginning of the period of crack propagation, and no evidence in these tests that the conditions during this period must be the same as during the induction period. Hence it is preferable to consider the mechanisms occurring in the two periods separately. There are several possibilities. For example:

1. The crack, probably initiated at a pit, propagates by continued anodic attack at the tip, under the influence of the corrodent (SCC).

2. The crack, once initiated, propagates under the influence of water or humidity, as in the work of Johnson and Willmer (124).

3. The crack, once initiated, propagates under the influence of adsorbed ions, as suggested by Uhlig for other systems (201).

4. The crack, initiated by a hydrogen embrittlement mechanism or otherwise, grows by a hydrogen embrittlement mechanism (HEC).

A combination of mechanisms is clearly possible, various processes contributing to, or reducing, the energy required for crack propagation.

4.4.3. The Induction Period. This period is regarded as the time required for a combination of conditions to develop conducive to the nucleation of a crack. Actually two consecutive periods may be included, if the convenient concept of an "active corrosion point" (section 4.2) is used.

1. Period during which features such as pits develop, some in the
notch, and one of which eventually forms an "active corrosion point" because of its location with regard to stress-concentration, surface or subsurface defects, and corrosion products.

(ii) Period during which this "point" develops, providing conditions for crack nucleation.

The period of crack propagation which follows is evidently short, so that variation in length of the induction period accounted for the scatter in stress-corrosion life. At first it was considered that stage (ii) was likely to be short, since some weakening of the test-piece would be expected but was not observed. As the ideas concerning the proposed hydrogen embrittlement mechanism are developed, it will appear that this stage occupied most of the induction period.

Within the range resulting from the element of chance, stress-corrosion life depended on strength level of the steel and on applied stress, probably through the effect of these factors on the notch sensitivity of the steel and on the rate of crack propagation.

The most obvious activity during stage (i) was the formation of corrosion pits, as indicated by the observed point formation of corrosion product. Only pitting at or very near the notch-root was of importance, since the lives of varnished test-pieces which had the notch-root only exposed and of uncoated test-pieces were within the same range. With cadmium-plated test-pieces, penetration of the coating and corrosion of the steel appeared necessary for crack initiation, although the formation of iron corrosion products could not always be seen.
The length of the induction period thus depends on when a suitably placed pit or other feature starts to form and on its rate of development. Rates of pit growth vary with a number of factors including the overall anodic activity if some measure of cathodic control prevails. This offers an explanation for the somewhat longer life when early general corrosion of the test-piece was observed.

4.4.4. Crack Initiation There was no indication during the tests of the initiation of the single crack causing failure of the test-piece. The usual association of the crack with a pit (through which it did not always pass) suggested one cause which might directly or indirectly start a crack. If no suitable pit had developed, some other feature, in conjunction with corrosion, might cause crack initiation first.

The crack is not necessarily nucleated at the surface if hydrogen embrittlement is involved; sub-surface initiation is probable, possibly at an inclusion located where triaxial stress is a maximum \((108,141)\).

The "active corrosion point" is an attractive and convenient concept, describing without defining a combination of conditions which, if it exists for a sufficient time, results in crack initiation. If the mechanism is SCC, such a point might represent merely a final stage of pit formation. Pits of a certain shape, as shown by Leu and Helle \((254)\) for stainless steels, might act as special stress-raisers. The "activity" of the point might then be purely mechanical \((230)\), or continuation of the same corrosion mechanism might give rise to a rapid directional anodic attack of the stressed steel. If the
mechanism is HEC, the mechanism occurring at the point is envisaged as making hydrogen available for rapid absorption by the stressed steel.

4.4.5. Period of Crack Propagation It has been assumed that after a crack has been initiated (i.e. nucleated and grown large enough to propagate), crack propagation is rapid, until almost instantaneous mechanical failure occurs. If crack propagation were slow, some evidence of additional cracks in test-pieces which had failed by stress-corrosion would be expected; also, some test-pieces which had been removed from the rigs before failure should have shown a definitely reduced breaking load when tested on the tensometer.

In connection with propagation rate, Brown and Beacham\(^{(230)}\) have commented that the rate of growth of pits (which they regarded only as stress-raisers) is several orders of magnitude less than the rate of crack propagation.

4.4.6. Proposed Mechanism

4.4.6.1. Initial Evidence. The reason for suggesting hydrogen embrittlement as the mechanism of corrosion-induced failure of high-strength steels under stress was the close similarity in characteristics with delayed failure due to hydrogen embrittlement. Comparison of Fig. 26 adapted from Fig. 12 of this thesis, with Fig. 27, redrawn from Troiano's papers\(^{(139,140)}\), illustrates the similarity of the applied stress versus life curves for the two phenomena. The upper and lower critical stresses of Troiano cannot be quite paralleled in stress-
FIG. 26. Stress-Corrosion Lives of Rex.539 Notched Test-pieces in 3% Sodium Chloride Solution. (adapted from Fig. 12)

FIG. 27. Static Fatigue Lives of Hydrogenated AISI 4340 Notched Test-pieces. (strength level 103 t.s.i.; notch sharp; hydrogenated, cadmium-plated and baked for 3 hours at 149°C) (after Troiano (139, 140))
corrosion, but the trends to very short life at high stress, very long life at low stress, and slight stress-dependence at intermediate stresses were observed.

A second point of similarity is the greater susceptibility (i.e., shorter life) for steels of higher strength level, and thirdly a lower susceptibility for a steel of higher silicon content. Rex.539 (1.5% Si) was less susceptible than En40C (0.3% Si) in the present stress-corrosion tests; steels of higher silicon content have been shown less susceptible to hydrogen embrittlement [109,110].

These points of similarity do not prove that corrosion-induced failure involves hydrogen embrittlement. It might be argued, for example, that both failure phenomena depend on the same mechanical properties of the steel, such as notch sensitivity, and hence must show similar characteristics. However, by assuming a hydrogen embrittlement mechanism, the results obtained in the investigation can be explained in detail.

4.4.6.2. Outline of Proposed Mechanism. It is assumed that hydrogen atoms, liberated by a cathodic reaction of the corrosion process, are adsorbed at the steel surface, and are then, under special conditions prevailing at the notch, absorbed by the steel. Diffusion to points of high stress-concentration results in the local accumulation of enough hydrogen to initiate a crack. The presence of a stress-concentration, e.g., the region of highest triaxial stress a little below the notch root, is essential to the mechanism, since by
the drawing of the hydrogen away from the surface further cathodic generation is stimulated.

4.4.6.3. Discussion of Proposed Mechanism. One of the objections sometimes raised against hydrogen embrittlement theories of stress-corrosion of steels in neutral media is that the cathodic potential available is not sufficient to provide the overpotential for the hydrogen evolution reaction when polarisation effects are taken into account. Even the lowered pH in corrosion pits is not expected to permit the reaction to occur (16). From the thermodynamic point of view, iron corroding in neutral solutions should just liberate hydrogen (15).

However, the evolution of hydrogen is not necessary; in fact, evolved hydrogen is not embrittling. All that is required is that the first stage of the hydrogen reaction should occur, to form hydrogen atoms adsorbed on the steel surface. Adsorbed hydrogen may also result from reaction of water adsorbed on the steel surface (81).

Adsorbed hydrogen is usually regarded as polarising the cathodes, so that corrosion cannot proceed unless the hydrogen is removed by evolution as gas or by reaction with a "depolarising agent", or, a third possibility, the steel may absorb the hydrogen. A cathodic overpotential is required for this to occur, corresponding to a very high gas equilibrium pressure (77), consequently hydrogen absorption is often accompanied by hydrogen evolution, although not necessarily so (84). Conversely, hydrogen evolution is not necessarily accompanied.
by hydrogen absorption.

Under the conditions of the present tests, the main overall cathodic reaction is, of course, the reduction of dissolved oxygen. Hydrogen absorption need only occur to a very limited extent, and very locally, and the process is more likely to compete with oxygen reduction where oxygen is less available, for example, at the notch-root, in pits and crevices. There is some analogy with the experiments of Bengough and Lee\(^{(19)}\), in which small amounts of hydrogen were evolved when steel corroded in aerated neutral solutions, but not in the absence of oxygen. It is quite likely that more hydrogen is produced at special sites under aerated conditions, which permit vigorous corrosion, than is produced over the whole surface under de-aerated conditions, where corrosion is negligible.

There are a number of factors in these tests which together may facilitate hydrogen absorption in embrittling quantities. Low alloy steels heat treated to high strength are more susceptible to hydrogen embrittlement than are softer steels, and even when unstressed have been shown to absorb hydrogen to significant bulk concentration from slightly acid acetate buffer solution under mild cathodic polarisation\(^{(94)}\). Stress, or at least plastic strain, appears to promote hydrogen absorption, probably by increasing the number of "traps" within the steel (2,3,6), so that it is likely that absorption will occur from neutral salt solutions without an applied cathodic
potential. The stress-concentration just beneath the notch root would serve as a trap. The "trapping" energy, of the order of 5 Kcal/mole, might be partly available to facilitate hydrogen absorption.

Stress makes most metals more anodic by a few millivolts, but for high strength steel a figure of 60 mV has been quoted. A stress gradient introduces a galvanic effect between the anodic highly stressed and less stressed metal. The importance of the notch, therefore, is that the concentration of anodic activity at its tip, by lowering potential, increases cathodic activity at adjacent points, just where there is least oxygen in the environment, and where hydrogen absorption should occur most readily. A similar situation has been used to explain rapid anodic attack at the tip of a growing crack during stress-corrosion cracking, but in the present case the emphasis is on the cathodic process because of the susceptibility of the material to hydrogen embrittlement, rather than on penetration by anodic dissolution.

The slightly lowered pH within pits would also assist, and effects analogous to the low hydrogen overvoltage of carbide particles might be useful.

The diffusion of hydrogen to the region of highest triaxial stress, just beneath the notch-root, forms part of hydrogen embrittlement and delayed failure theory, summarised in 2.5.3. The theories developed by Troiano and his co-workers seem most applicable to the present work, particularly because they were derived from experiments.
on ultra-high strength steels. The alternative, that hydrogen embrittles by discharge into, or adsorption on micro-cracks or other voids would serve fairly well, provided that such defects attract hydrogen more strongly when located at stress concentrations. Crack nucleation at an inclusion has been proposed in connection with both hydrogen embrittlement (108) and stress-corrosion (223) of high strength steels. (The inclusion could be regarded as a stress-raiser or as a micro-crack).

Hewitt's comment (66) that hydrogen taken up when test-pieces were charged under stress would diffuse directly to stress-concentrations and Troiano's observation (139, 140) that very small amounts of freshly absorbed hydrogen could embrittle ultra-high strength steels are relevant in connection with the mechanism under discussion.

Once a crack has nucleated, it would be expected to grow quickly outwards through a hydrogen-containing region to the notch-root, the inward propagation of the crack being probably slower and controlled by hydrogen diffusion. The whole propagation process can occupy a time only of the order of minutes unless the very short lives observed result from an independent mechanism. The roughly semi-circular areas on the fracture surfaces representing the stress-corrosion crack generally have radii between 0.3 and 0.5 mm., so that the rate of crack propagation would be about 0.05 mm. per minute.

This rate appears reasonable when comparison is made with the
results of Johnson, Morlet and Troiano \(^{(142, 139)}\). From their photographs of fractures, it seems that hydrogen-controlled cracks can propagate to depths of 0.5 to 1 mm in 20 to 60 minutes, this time including the incubation period.

4.4.7. Further Development of Hydrogen Embrittlement Mechanism

4.4.7.1. Additional Evidence The mechanism proposed in 4.4.6. was based on a consideration of the general trends of stress-corrosion lives, with 3% sodium chloride solution as corrodent. Other observations made in the course of testing can be explained by the hydrogen embrittlement theory, or can be used to fill in details of the mechanism.

4.4.7.2. Stress without Corrosion Long periods under stress without applied corrodent resulted in no significant change in strength or stress-corrosion life (3.4.3.). Evidently there were no ageing effects, nor did incipient cracks form.

4.4.7.3. Corrosion without Stress If the main process occurring during the induction period were simple pitting, previous corrosion would be expected to shorten life by a time equivalent to the depth of pits produced. No appreciable shortening was observed (3.4.3.), and in this respect the system under investigation differed from stainless steels in chloride solutions \(^{(181)}\) and mild steels in nitrates \(^{(255)}\), where stress during the induction period is unimportant.

Clearly, processes other than simple pitting occur at the notch early in the induction period. The stress concentration may serve to
localise and accelerate pitting, and "active corrosion points" (and thus hydrogen absorption) may exist during most of the induction period, even if only functioning slowly. Without stress, hydrogen absorption would be most unlikely to occur.

4.4.7.4 NTS during Induction Period

The failure to detect a drop in NTS, as determined on the tensometer, during the induction period may indicate that hydrogen uptake rate increases with time (pitting being autocatalytic, and the accumulation of hydrogen increasing the stress at the sub-surface stress concentration), and that a critical hydrogen concentration is only attained shortly before crack initiation. However a better reason why no drop in NTS was observed can be based on the demonstration by Johnson, Morlet and Troiano (142) that hydrogen diffusing up a stress gradient would disperse again when the stress was removed. The time interval between unloading a test-piece and breaking it on the tensometer was normally an hour or more, and the hydrogen could not re-concentrate during the few minutes of the tensile test.

Determination of NTS without unloading from the rig should have shown a reduction. Such observations were actually made, but their significance missed, during the earlier testing work. Attempts to increase stress from 50% to 70% NTS during stress-corrosion tests resulted in fracture before or shortly after the higher stress was attained (3.4.3).

It may be significant that the NTS determined after a period of
stress-corrosion was always just below the original NTS, whereas after a long sustained load test, the NTS figures varied below and above. Possibly a little hydrogen remained at or near the notch-root, and a slight weakening resulted.

4.4.7.5 Period of Hydrogen Absorption It was originally suggested that hydrogen was taken up only towards the end of the induction period from "active corrosion points", which developed after a variable period of time, thus explaining scatter of stress-corrosion lives. However, the evidence for this is no longer valid in view of the discussion in the last two sections. It is more likely that hydrogen was absorbed during most of the induction period, at a rate depending on the activity and distribution of pits or other surface features in relation to the distribution of inclusions just beneath the notch-root. In tests at 70% NTS, the hydrogen uptake may be a little faster, and the critical concentration for crack initiation a little lower than in tests at 50% NTS.

4.4.7.6 Very Short Lives A few test-pieces in each batch had very short lives, as defined in section 3.9.2, (points 3 and 7 for Rex.539 and En.40C respectively). Their significance is difficult to assess. No evidence of a different mechanism of failure was found, and no abnormalities were noted before testing. However, some special conditions of the notch, possibly an arrangement of cracks or inclusions, must be assumed to account for a rapid hydrogen absorption when an active corrodonent was applied.
It is difficult to accept that a surface inclusion, groove, or other defect could cause such a rapid uptake of hydrogen from a neutral solution to initiate and propagate a crack in a few minutes, and the presence of a "pre-crack" does not provide a satisfactory explanation, since the crack would be expected to grow in the presence of the "inactive corrodents", and no such observation was made (see 4.4.10).

The presence of a sub-surface crack at or near the point of maximum triaxial stress could explain most of the features. As the surface itself is intact, an "active corrodent" would be needed. The stress field set up by the crack would probably accelerate hydrogen uptake to some extent.

The remarks concerning cadmium-plated test-pieces in 4.5.5 fit in well with this idea, and also the observation that the appearance of the fracture was no different from the fracture occurring after a normal life.

The very short life includes time for hydrogen absorption and crack propagation, and gives an indication of crack propagation rate (see end of 4.4.6.3.) Even more rapid failure can be produced by cathodic charging under stress (3.8.1.), but in this case hydrogen absorption would have been more intensive and over a greater surface area.

One of the two batches of En.40C test-pieces, D1, showed a greater tendency to a very short life, suggesting a connection with the exact conditions of machining. Certainly a blunt tool gave non-standard results in one instance. Surface stresses at the notch were suspected.
4.4.3. Restatement of Hydrogen Embrittlement Mechanism  A mechanism was proposed in 4.4.3 and 4.4.6 as a basis for discussion. The stress-corrosion life can still be regarded as of two periods, a long induction period and a short period of crack propagation, but details of the former must be modified for reasons arising from the discussion in 4.4.7.

The several stages leading up to crack initiation, controlled crack propagation and final mechanical failure can then be stated as follows:

(i) An initial relatively short stage of simple pitting, which might be affected by prior corrosion without appreciably shortening stress-corrosion life,

(ii) The main stage, of hydrogen absorption at the notch, certain pits increasing or changing their activity under the influence of stress. The rate of absorption may increase with time. It depends on the number and activity of the pits involved, and is controlled by the diffusion of hydrogen to subsurface stress concentrations. The diffusion rate depends on stress-gradient and on hydrogen concentration gradient, and the latter in turn on cathodic overpotential and thus on pit activity. Strength is not permanently impaired.

(iii) Possibly a short stage distinguished by permanent damage as the hydrogen concentration approaches the critical value. (Permanent damage due to severe hydrogenation has been observed, for example by...
Bastien\(^{(69)}\). Crack initiation and propagation follow.

In section 4.4.3, no particular mechanism was considered, but the comments there are still applicable, except that now variation in life must be attributed to variation in the rate of hydrogen uptake near to the point of eventual crack nucleation.

Hydrogen may be absorbed elsewhere at the notch root, and would diffuse to various features in the zone of highest triaxial stress. The crack would arise where the hydrogen concentration first became critical. Only in the rare event of a second crack starting during the short propagation time of the first would two primary fracture areas be apparent.

4.4.9. **Comparison with Other Mechanisms**. The mechanism proposed in 4.4.6 to 4.4.8 accounts for the observed characteristics of the corrosion-induced failure satisfactorily, and it has been argued that hydrogen absorption as a result of a corrosion reaction is not so unlikely as electrochemical principles alone would suggest.

Other mechanisms may be based on localised anodic attack, combined with stress and strain effects. Such mechanisms have been discussed in 2.6.3. Stress-assisted intergranular corrosion is not usually considered for high strength steels, since localised corrosion at prior-austenite boundaries is not a feature of their corrosion behaviour. Pitting attack is an obvious starting point, and has been accepted by several authors e.g. Tinar and Gilpin\(^{(229)}\) and Brown and Beacham\(^{(230)}\). Crack initiation would be expected when a pit at the
notch-root reached a critical depth, and crack growth would follow by the process of anodic attack of the yielding or highly stressed metal at the crack-tip, or by some electrochemical/mechanical process or by some other mechanism. (Brown and Beacham have made some calculations regarding critical stress concentrations for a pit to nucleate a crack and for a crack to propagate).

There are difficulties in explaining some of the observations and results by a simple pitting mechanism. Since no reduction of NTS was observed prior to stress-corrosion failure, it must be assumed that the whole weakening and fracture process occurs within a short space of time, and hence that the rate of growth of pits, or at least of one pit, increases rapidly towards the end of the test-piece life. If the growth rate were steady through-out the induction period, when test-pieces were removed from the rigs before failure and tested on the tensometer, cracks should have initiated with increasing stress, and also have propagated unless the presence of wet corroden is essential to crack propagation. Hence some reduction of NTS should have been recorded. The hydrogen embrittlement theory provides a simple explanation.

An accelerating pit growth rate might be explained by the increasing stress-concentration at the pit bottom. Whether or not this acceleration occurs, stress-corrosion life should depend on any factor affecting the rate of pitting. Hence the frequency of application of corroden, by changing the relative periods during which the test-
pieces were wet and dry, and the ambient conditions, by controlling rate of evaporation, should have affected life. Similarly, life with sodium sulphate as corrodent should have been longer than with sodium chloride, since pitting in chloride solutions is normally more rapid than in sulphates (26). The life range was found not to be affected by these variables. (By contrast, the cadmium-plated test-pieces had longer lives with sodium sulphate, the prerequisite for cracking being penetration of the coating by the corrodent).

In the hydrogen embrittlement mechanism, the important factor is not pit depth, but the development of "active corrosion points"; then the rate at which hydrogen can enter and diffuse in the steel controls the time to initiate the crack, and the effect of the frequency of spraying with corrodent is less direct. The time lag between generation of hydrogen by corrosion and the arrival of the hydrogen at the stress-concentration explains also why there was no preferred interval between the last application of the corrodent and fracture.

An anodic attack mechanism for crack initiation and propagation does not explain this point satisfactorily. Crack initiation would be expected when the test-piece was still wet, and although moisture might remain in the crack when the test-piece had dried superficially, propagation to fracture would still be more likely within a few hours of application of the corrodent. It is difficult to accept that the growing crack can "yawn" sufficiently to allow ready access of corrodent
to the crack tip as evidently occurs with more ductile materials.\textsuperscript{(16)} Alternating anodic attack and mechanical fracture might provide an explanation, a small amount of corrodent giving sufficient attack to start a short mechanical crack. However repetition of the cycle would be unlikely when the test-piece was dry; crack propagation in dry test-pieces evidently did not occur in tensometer tests at stresses below the NTS.

Two other observations favour the hydrogen embrittlement mechanism. There was no evidence of corrosion product on the fracture surfaces, except where splashing had occurred after fracture, so it is unlikely that corrodent entered the crack at all. Secondly, the pit which seemed responsible for the stress-corrosion crack often was not quite at the notch-root, and the fracture did not pass through the pit. Sub-surface crack initiation is the simplest explanation. The alternative is initiation at a surface defect at which no visible point of corrosion product was formed.

4.4.10. Note on Crack Propagation The greater part of the discussion has been concerned with the processes leading to sub-surface initiation of a crack when the amount of hydrogen at a stress-concentration reaches a critical level. It is often tacitly assumed in discussions of stress-corrosion that the processes causing crack initiation and crack propagation are similar in nature, and this has been done here.

However, when the crack has grown outward to reach the surface,
further inward propagation could be facilitated by several processes (see 4.4.2.). Simple mechanical failure can probably be excluded, since the primary fracture area was distinguishable from the rest of the fracture surface. Rapid anodic attack at the crack tip can also be excluded for reasons given in the last section.

A process involving reduction of the energy associated with the formation of new crack surfaces by adsorption appears to be more likely. Adsorption of specific ions may be rejected on the grounds that chlorides and sulphates behave alike, but adsorption of water from either the liquid or vapour phase could effect crack propagation. Fractures would be expected to be more frequent when the test-pieces were wet, unless atmospheric humidity could maintain propagation. An explanation of the very short lives might be based on an adsorption process, the test-pieces being assumed pre-cracked, but it has been noted that there were no very short lives with the inactive corrodents, nor during atmospheric exposure alone.

There remains the obvious process of crack propagation controlled by hydrogen diffusion to the growing crack tip. If sufficient hydrogen is already in the test-pieces, there is no need of further reaction with the environment. However the presence of the corrodent during crack propagation might make additional hydrogen rapidly available. Rapid absorption of hydrogen in the presence of surface cracks was one suggestion made in connection with very short lives. Humidity in the growing crack may assist propagation, water, or possibly hydrogen, being
adsorbed on the fresh crack surfaces. (In this connection, see Hanna et al.\(^{231}\). It is also of interest that the mechanism of embrittlement by hydrogen may involve a weakening of lattice bonding \(^{137}\), the process being continued by adsorption of hydrogen on the crack faces \(^{123,201}\).)

### 4.4.1. Summary of Discussion

Two main alternative mechanisms have been discussed as explanation of the stress-corrosion test results on uncoated ultra-high strength steels in neutral salt solutions. Both mechanisms involve localised anodic attack - pit formation - during the induction period, the significant pits being at the notch-root, but they differ in the processes of crack initiation and propagation. In the proposed mechanism, cracking is attributed to hydrogen embrittlement arising from special corrosion conditions at the notch-root; the observed behaviour can be explained quite well by accepted hydrogen embrittlement theory. The alternative mechanism explains the broad pattern of results but the crack propagation mechanism has not been defined for lack of evidence both in the present work and in the literature (presumably alternate anodic attack and mechanical fracture would explain the propagation rate); also a number of assumptions are needed to fit the more detailed observations, and contradictions arise. For example crack propagation is assumed to proceed when the test-piece is superficially dry in connection with stress-corrosion fracture; the opposite assumption is used to explain why no drop in NTS was observed prior to stress-corrosion failure. (The observation, by Tiner and Gilpin\(^{229}\),
of non-propagating micro-cracks during the stress-corrosion of martensitic steel might help to explain this point.)

4.5. Discussion of Other Observations and Results

4.5.1. General Comments A mechanism of stress-corrosion cracking for high strength steels has been proposed, and from the results of tests with uncoated notched test-pieces in sodium chloride and sodium sulphate solutions some details of the mechanism have been worked out.

It now remains to consider the other observations and results and to fit them into the scheme as far as possible.

4.5.2. The "Inactive Corrodents" (Table VI) The results were briefly discussed in 3.4.6.1., and some generalisations attempted. Although these solutions - water, ammonium carbonate, potassium chromate and dichromate - did not cause cracking in eight weeks, some reduction in strength and in subsequent stress-corrosion life was noted. There was no evidence of a "very short life" phenomenon.

The results with ammonium carbonate are of little interest. The effect on stress-corrosion life was indicated but not established by the few tests made.

However the chromate and dichromate solutions appeared to have consistent effects, depending on stress level, and more noticeable for the more sensitive En 40C steel. At 50% NTS, the increase in subsequent stress-corrosion life may be due to a passivating effect of the chromate. Possibly at 70% NTS, the more anodic notch-root would not be passivated, and thus subsequent life reduced by a galvanic effect, but this would
not explain the reduction of NTS. From consideration of the theories of stress-corrosion cracking based on critical passivation or on oxide film rupture by strain, as described by Smialowski (200), Logan (206), and others, the formation of sharp pits or even micro-cracks at the notch-root might be suggested. Those would act as stress-raisers, and also serve as sources of special pits when sodium chloride solution was later applied.

Extending these speculations one stage further, stress-corrosion cracking might occur eventually in chromate solutions, at a stress of 70% NTS but not at 50% NTS, by a mechanism not involving hydrogen embrittlement. Since corrosion is slight, and the chromate ion is a cathodic depolariser it would not be expected that hydrogen would be available for absorption by the steel.

4.5.3. Tests with Slightly Alkaline Sodium Chloride (Section 3.4.6.3.) These tests were not pursued to any great extent, and may be regarded as control tests. The pH of the solutions was determined by indicator papers, and can be taken as pH9. More alkaline solutions were not used, in order to avoid changing the character of the corrosion process, hydroxyl ions catalysing the anodic reaction (22).

It is believed that the comments made in 3.4.6.3. on increased stress-corrosion life, especially at the higher stress, are valid. The interpretation in terms of mechanism is ambiguous:—

(a) The general corrosion rate may have been reduced, because the corrosion product (ferrous hydroxide) was less soluble in the
solutions of higher pH. This would increase stress-corrosion life by any mechanism.

(b) The higher pH is equivalent to a reduction in hydrogen ion concentration of about two orders of magnitude, and thus the rate of hydrogen absorption by the steel would be reduced. If in neutral chloride solution the control of hydrogen uptake were by the rate of stress-induced diffusion in the steel, limitation of hydrogen uptake by reduction of hydrogen ion concentration would affect tests at the higher stress to a greater extent.

4.5.4. Tests with Sodium Chloride/Potassium Chromate Mixtures  The results were given in Table VIII and Fig. 16, and the stress-corrosion life trends, in comparison with similar tests in sodium chloride alone, were outlined in 3.4.6.4. There was also some discussion in 4.4.1.

The objects of those tests were to investigate inhibitor action on stress-corrosion, and also to seek evidence on mechanism, the anticipated effect being similar to that of applied anodic polarisation. The solutions used had chromate:chloride ratios well in the range giving "corrosion" rather than "passivation", as indicated by the empirical expression of Matsuda and Uhlig (34), so that the stress-corrosion mechanism of the sodium chloride tests should still be applicable. (This expression was derived for solutions one to three orders of magnitude more dilute than those used here.) Extrapolated, it indicates that 2250 g/1 potassium chromate would be required to inhibit 3% sodium chloride; 10% potassium chromate would just inhibit
Assuming that the corrosion process is under some measure of cathodic control, chromate ions can enter into the system in several ways:

(a) by cathodic depolarisation, reinforcing the effect of oxygen, and so stimulating the anodic reaction.

(b) by anodic passivation, by direct action of chromate, or by over stimulation of the anodic areas, as discussed in 2.2.2.

(c) following from (a) by reducing the availability of hydrogen for absorption by the steel, adsorbed hydrogen reacting with chromate.

At first examination, the results seemed to indicate a purely anodic stress-corrosion mechanism. The reduced life in the solution of lowest chromate:chloride ratio can be explained by process (a), and the longer life in higher chromate solutions by process (b). On further consideration, the situation becomes less clear cut; the special conditions at the notch have been neglected. A hydrogen embrittlement mechanism is not necessarily invalidated, and even for a purely anodic mechanism it does not follow that changes of overall anodic activity must be reflected in similar changes in stress-corrosion rate. From the ideas of Evans on "dangerous" anodic inhibitors (30), it appears more likely that with increasing chromate:chloride ratios an intensified anodic attack at the notch-root would result, although the total corrosion reaction would diminish. Thus stress-corrosion should be stimulated until the ratio was well in excess of the critical ratio for inhibition
of corrosion, but the effect of the variation of the ratio on total life would depend on the relative importance of the several stages leading to final fracture.

Now considering the proposed hydrogen embrittlement theory, it must be emphasised that the hydrogen absorbed by the steel represents only a minor product of cathodic action, and that the amount available for absorption depends both on the rate of corrosion at the notch-root, and on competition between the oxygen reduction reaction and hydrogen absorption. It is suggested that with lower chromate-chloride ratio, process (a) preponderated, and the faster anodic reaction resulted in an increased cathodic overpotential locally, and hence faster hydrogen absorption. With higher ratio, process (c) was faster, and on balance hydrogen was absorbed more slowly.

Another possibility is that stage (i) (see 4.4.8) is of greater importance than previously suggested.

4.5.5. Cadmium-coated Test-pieces (Corrodent 3% NaCl) The results under discussion were given in section 3.6, and compared with the results on uncoated test-pieces. The main points were summarised in 3.9.2, (16 to 20, 23).

The interpretation of the results in terms of stress-corrosion mechanism is complicated by the several possible functions of the cadmium. When of adequate thickness and quality, the coating prevents access of corrodent to the steel, and it appears that corrosion of the cadmium does not initiate stress-corrosion failure. At defects in the
coating, the cadmium should protect the steel cathodically, but in so
doing may encourage hydrogen absorption by the steel. Thus stress-
corrosion life is likely to be increased by a good cadmium coating, but
if the coating is defective, particularly at the notch of the test-piece,
rapid cracking by a hydrogen embrittlement mechanism may result.

A curious feature was that very short lives occurred at 50% NTS
but not at 70% NTS. The frequency of very short lives was understandably
reduced by the cadmium coatings on Rex.539 (compare batch A1 of Tables
IV and X), unless the 8 hour life (Table X) should be classified as a
very short life with failure delayed by the cadmium as a barrier to the
corrodent. The thinner coatings on En.40C both increased the frequency
and decreased the lengths of the very short lives (compare Tables V
and XI), and evidently the exceedingly thin and probably porous layer
of cadmium at the notch-root did not obscure the conditions for very
short life, but on the contrary increased the chances of such conditions
existing. The more rapid failure can be attributed to faster hydrogen
uptake due to galvanic action between the cadmium and the steel.

The absence of very short lives at 70% NTS might be explained on the
lines that the highly stressed notch-roots were more anodic still than at
50% NTS, and that the reduced galvanic effect between the steel notch-root
and the cadmium lessened the opportunity for vigorous local cell action.

Considering now "normal" lives, there was a tendency for lives at
50% NTS to be a little shorter than at 70% NTS (compare batches A1 and
A2 of Table X), although the longest lives were the same for both stress
levels. However the same was not true of the batch C test-pieces, presumably because the two-layer coatings were more protective. The cadmium first corroded, thus protecting the steel at porosities, except at the notch-root where some pitting of the steel may have occurred. Evidence for this was the appearance of small patches of ferric corrosion products a few days before failure. Pitting may have proceeded for some time before iron products, contrasting in colour with the white cadmium product, appeared at the surface, and accordingly in shorter tests (say, failure in less than 400 hours) ferric products were not always observed. Pit formation preceding cracking does not necessarily indicate that the anodic reaction is the main cause of cracking but only that the steel is exposed to the environment under such conditions that local corrosion cells can develop.

On the whole, these tests support a hydrogen embrittlement mechanism, the most interesting results being concerned with very short lives.

4.5.6. Cadmium-coated Test-pieces (Other corrodents) The results given in 3.6.3 need little further discussion. Clearly chromates, even in the presence of chloride, inhibited corrosion and the inhibition persisted. The loss of NTS after prolonged testing is in keeping with the effect of chromate solutions on uncoated test-pieces. Probably a stress-corrosion process of different and slower mechanism was involved; alternatively stage (iii) of the hydrogen embrittlement mechanism had been reached, but the shape of the fracture surface did not
4.6. Discussion of Evidence on Mechanism in Literature.

Processes which may be responsible for the stress-corrosion cracking of high strength steels were briefly discussed in 4.1. and 4.4.2.

These processes, SCC, HEC and SSC, are not mutually exclusive, and may occur together or even in sequence. For a particular set of conditions, the fastest would provide the main cracking process. It is conceivable that one process might set the conditions for cracking after which another process might take precedence. As Coleman et al. (123) pointed out in discussing their adsorption mechanism, the clear association between electrochemistry and stress-corrosion does not necessarily prove that the cracking process itself is electrochemical. The mechanism proposed in the present work might be regarded in a similar way.

Considering high strength steels more specifically, there is little doubt that in acid media, and in neutral media under sufficient cathodic polarisation, the process is HEC. In comparative tests, these conditions (sometimes with sulphides present also) have been used to provide "HEC standards". Studies of stress-corrosion cracks, in neutral salt solutions, compared with "HEC standards" have not provided conclusive evidence for a SCC or HEC mechanism. The crack path is intergranular (prior austenite boundaries) in each case (222 to 225). Detailed observations only indicate differences in degree. For
example, the observation that for horseshoe-type test-pieces only one crack forms in sodium chloride solution but more numerous cracks develop in hydrochloric acid\(^{(223)}\) may only confirm that a more critical combination of conditions is required for hydrogen absorption and crack initiation in neutral solutions.

The effects of imposed polarisation on stress-corrosion life have shown the importance of the anodic reaction in neutral salt solutions\(^{(221, 224, 236)}\), and it has been concluded that the mechanism is SCC rather than HEC, since the life without polarisation lies to the anodic side of the maximum - typical curves are reproduced in Fig.28.

For more severe conditions of cathodic and anodic polarisations, there is no dispute that cracking is by HEC and SCC respectively. Davis\(^{(222)}\) pointed out differences in crack form (but not in crack path). Under conditions where there is no overriding factor, it is quite possible that a number of factors in combination determine which mechanism prevails. Such factors might be the presence or absence of a notch, surface finish, steel structure and strength level, or even stress level. Higher strength evidently favours hydrogen embrittlement in both ultra-high strength steels\(^{(227)}\) and in the martensitic stainless steels\(^{(236, 229)}\). An example is the susceptibility to cracking of martensitic ultra-high strength steel in water, as in sodium sulphate solution, in the experiments of Yamaoka and Wranglan\(^{(227)}\), who attributed the cracking to hydrogen embrittlement. Water did not crack the tempered martensite in the present work.
Fig. 28. Curves showing the effect of applied current and impressed potential on stress-corrosion life in aerated 3% NaCl solution.

Redrawn from Phelps and Longinow (221) and Hughes et al. (224) respectively.
Thus, in brief, although some of the published work on the stress-corrosion of ultra-high strength steels appears at first sight to contradict the mechanism proposed here, there is no real contradiction when the special conditions at the notch of the test-piece are taken into account. The remarks made in 4.5.4. (p.197) are applicable; a mild cathodic polarisation, by reducing the difference in potential between the highly stressed notch-root and the rest of the surface, might have resulted in less localised hydrogen being available for absorption.

The work of Hanna, Troiano and Steigerwald\(^{(231)}\) confirms the ideas expressed here. They used tempered martensitic steels, notched and pre-cracked, and because of the severe stress conditions, failure was induced by water alone. They considered that the observed characteristics gave ample evidence of hydrogen embrittlement, much as has been done in the present discussion.

4.7. **Steel Structure and Composition**

Little attention was paid to details of steel structure. The main difference between the two steels investigated was the higher silicon content of Rex. 539. This resulted in a higher tempering temperature for a given UTS, and, to judge from the results of Reisdorf\(^{(107)}\), a retention of \(\varepsilon\)-carbide. For En.40C, most of the \(\varepsilon\)-carbide should have transformed to cementite during tempering.

The lower sensitivity of Rex.539 to stress-corrosion is in keeping with the lower susceptibility of silicon-rich steels to hydrogen
embrittlement (109,110). The explanation may lie in the higher tempering temperature of Rex.539, giving a more stable or more stress-free structure, but the presence of ε-carbide gives a more satisfactory explanation (cf. 257). Assuming that this carbide has the affinity for hydrogen indicated by Owe Berg's synthesis (108), it would increase the amount of hydrogen entering the steel but its main action would be to trap hydrogen, and hence a longer time would be required to build up the critical concentration of hydrogen near the notch-root.

Differences in corrosion rate or habit do not explain the differing susceptibilities to stress-corrosion, since it was not possible to correlate life with corrosion observations.

It is interesting that in the work of Hanna et al. (231), the silicon-rich 330M steel did not differ markedly in susceptibility from AISI 4340. Presumably, the trapping effect of the pre-existing crack exceeded that of the ε-carbide, assuming, with Hanna et al., that the mechanism under those conditions is HEC.

The microstructures of Rex.539 and En.40C were illustrated on page 152. En.40C retained some martensitic pattern, and this may account to some extent for its greater susceptibility to a cracking process based on hydrogen embrittlement.
5. **FINAL SUMMARY AND CONCLUSIONS**

5.1. **General Observations** The stress-corrosion cracking of two ultra-high tensile steels (UTS 110 to 125 ksi) was investigated. Notched test-pieces stressed in tension at 50 to 70% of their breaking stress (NTS) cracked within about three weeks when aerated neutral solutions (NaCl, KCl, Na₂SO₄) were applied daily. Exposure to air of varying humidity, to water, or to less corrosive solutions, including chromates, produced no fracture during the 6 to 8 weeks duration of the tests; chloride/chromate mixtures were similar in effect to chloride solutions.

Test-pieces stressed at 33% NTS and exposed to chloride solution did not fail in 6 weeks; at 80% NTS failure was much more rapid, life being about 1 hour for Rex.539 test-pieces.

Times-to-fail (life) varied widely in replicate experiments, and this appeared to be a feature of the system. The three corroding agents were equally effective, and increasing the frequency of application made little or no difference to the life range. Some very short lives were considered outside the usual life range.

Taking "susceptibility" as indicated by life range or average log. life, the steel Rex.539 was far less susceptible than En.40C. Susceptibility was greater for higher strength levels, but possibly only because of the greater load for a given NTS. Since life was not greatly affected by stress in the range 50 - 70% NTS, it was not possible to reach strict conclusions on this point.
The presence of the notch (i.e., stress concentration) seemed all important to the stress-corrosion process; plain tensile specimens did not crack. The experiments with lacquered test-pieces (3.8.2.) showed that all the necessary action could be confined to the notch-root. The extent of general corrosion on uncoated test-pieces could vary widely during the stress-corrosion life, and also corrosion in the absence of stress had no effect on subsequent life, from which it follows that corrosion remote from the stress-concentration, or corrosion in the absence of stress, has little to do with the process leading to cracking.

5.2. Stress-corrosion Mechanism Other, more specific, observations indicating the mechanism of crack initiation are:

(1) The stress/life relationship is similar to that for the delayed failure of hydrogen-charged high strength steels (139), and unlike those for many SCC systems - e.g. the hyperbolic relationship of Azhagin (150), and the logarithmic relationship of others (181, 236, 256).

(2) There was no or very slight permanent reduction in strength during the incubation period, but an increase in stress towards the end of that period (while still in the rig) usually resulted in immediate or early failure, (4.4.7.4.). This behaviour suggests hydrogen embrittlement (142, 231).

(3) There was only one primary fracture area. If a number of cracks were propagating, indication of other primary fracture areas, or
additional cracks, would have been expected; the final rapid mechanical failure would not distinguish sub-critically hydrogen embrittled metal.

(4) The primary fracture area was evidently not corroded prior to fracture, and did not always pass through a corrosion pit.

(5) The silicon-containing Rex.539 was less susceptible than En.40C.

(6) Pits produced by corrosion alone did not affect strength or subsequent stress-corrosion life.

(7) Sodium sulphate and chloride were equally effective corrodents.

(8) Cadmium-plating, when inadequate at the notch, reduced the stress-corrosion life (4.5.5*).

(9) There was no preferred interval between the time of last application of corrodent and of final failure.

The preceding observations can best be explained in terms of hydrogen embrittlement. Hydrogen is absorbed as a by-product of the corrosion reaction only when the test-piece is under stress, and probably only near the notch-root. During the relatively long induction period, hydrogen diffuses to where the triaxial stress is a maximum just beneath the notch-root surface. Very shortly before final failure, a subsurface crack nucleates at one point, and propagates rapidly. The actual point of nucleation may be an inclusion suitably placed; in the case of very short lives, it is suggested that there is a pre-existing micro-crack just beneath the surface.
5.3. Comment on Mechanism

It is known that very small amounts of hydrogen, freshly taken up, will embrittle a notched test-piece (139), so that it is only necessary that a small part of the corrosion reaction in the stress-corrosion tests provides hydrogen for absorption at the notch-root. An active corrosion reaction is required, and this is provided by the ready supply of oxygen and by an adequately conducting electrolyte. With these points in mind, the results of the tests with mixtures of sodium chloride and potassium chromate can be explained in terms of the hydrogen embrittlement mechanism for the special case of notched tensile test-pieces. The special conditions at the notch-root, especially the stress-concentration just beneath the surface to which hydrogen is drawn, favour the uptake of hydrogen there, and corrosion reactions over the rest of the test-piece surface have only indirect influence on cracking.

It might be said that when notched test-pieces, known for their sensitivity to hydrogen embrittlement, were selected in steels known to be susceptible, it was inevitable that the hydrogen aspects of stress-corrosion would become more prominent. In the event, hydrogen embrittlement seems to have become the controlling process, producing failure more rapidly than anodic attack under the conditions of test.

It is a reasonable conclusion from the present work and the literature that the hydrogen embrittlement mechanism will only operate to completion if the steel has an untempered martensitic structure or if a notch or similar feature is present.
The very slight reduction in NTS near the end of the induction period (with active corroding agents) may be insignificant or may represent the effect of a small amount of hydrogen remaining near the notch-root at the time of testing. An alternative possibility is that a slow SCC process operates in parallel with HEC, and is responsible for the slight weakening. Such a process may explain the greater loss of strength in chromate solutions.

5.4 Practical Considerations. Ultra-high (and even high) strength steels are known to fail by stress-corrosion in service, as well as being susceptible to delayed failure attributed to prior hydrogen absorption. There may be several stress-corrosion processes contributing to the case histories of failures, the operating process depending on the circumstances.

The cracking process studied here is related to delayed failure by hydrogen embrittlement. It would become effective in steels at "ultra-high" strength, where there is a sharp stress-gradient, and particularly where a stress-concentration results. Intermittent exposure to a neutral corroding agent, such as an occasional splash with sea-water, would be sufficient to produce cracking, but if the stress is intermittent, and if the hydrogen can disperse into an adequate bulk of metal during the period unstressed, failure might be almost indefinitely postponed. Of course, failure by another mechanism might intervene, as might also happen if a continuous stress-concentration is not severe, e.g. in bent strip test-pieces. A continuously applied corroding agent, which increased cracking rate
but slightly in the present tests, might increase an SCC rate more markedly. The problem of corrosion-induced hydrogen embrittlement cracking should not be too serious, provided that notch-like stress-concentrations and defects are eliminated by design and inspection. Preferably a silicon rich steel should be used. Protective coatings can prevent or postpone cracking, but there is a risk that if a coating weakness coincides with a stress-concentration, cracking may be accelerated. An example of this is the behaviour of poorly coated cadmium-plated test-pieces. Organic coatings, such as the lacquer used in some of the experiments, could be very effective and would tend to be thicker at critical points, but a scratch through the coating at the notch was shown to result in rapid failure.

Preventive measures such as inhibitor additions or applied polarisations might be effective if carefully and properly applied, but they could be dangerous if misapplied. The over-all effect on cracking would depend on the relative effects on the total corrosion and on the proportion of the corrosion reaction producing hydrogen for absorption at the notch.

5.5. Suggested Further Work A number of lines of investigation are given below, which would help to confirm or add to the conclusions reached. Notched test-pieces are understood in each, stressed in tension.

(1) By rinsing test-pieces thoroughly after an estimated incubation period, and leaving them dry or wet with water alone, evidence for
the minimum conditions for crack propagation could be obtained. This would be preferable to using "pre-cracked" test-pieces.

(2) By applying corrodent less frequently, or by washing it off soon after application, the minimum corrosion/corrosion-free ratio which did not increase life range could be established.

(3) By intermittent stressing, the "reversibility" of hydrogen diffusion could be checked.

(4) Longer tests at 33% NTS or lower, and tests with steels at lower strength levels, and notches of various acuities, to examine limits of the stress-corrosion process.

(5) Tests with steels at several strength levels and at loads over a range to clarify in which sense steels of higher strength have greater susceptibility.

(6) Experiments on the effect of pH.

(7) Experiments with other solutions, e.g. nitrates, chlorates, phosphates.

(8) Experiments with chromate/chloride solutions to determine critical concentrations for cracking, with varying strength and stress levels. (Similarly, chromate/sulphate, nitrite/chloride or other mixtures).

(9) Polarisation experiments. (A cottonwool pad might be used as in the cathodic charging experiments).

(10) Experiments in which the notch-root is protected by a lacquer
to check whether embrittlement can arise at the notch due to corrosion further away.

Experiment series combining several of these lines (e.g. 4 with 7) would give added information. Comparative long tests with plain or shallowly-notched test-pieces, using the cottonwool pad method for applying corrodent, would help to establish whether HEC and SCC processes do proceed together, but at different rates.
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APPENDIX

I. Calculation of Notch Root Radius.

Consider a notch of width \( w \), depth \( d \), root radius \( r \), and angle \( 2A \), as the diagram above.

Then, \( d = XQ = XP - QP \) in which \( XP = \frac{1}{2}w \cdot \cot A \)

and \( QP = OP - OQ = r \cdot \csc A - r \)

Hence, \( d = \frac{1}{2}w \cdot \cot A - r(\csc A - 1) \)

Rearranging, \( r = \frac{\frac{1}{2}w \cdot \cot A - d}{\csc A - 1} = \frac{\frac{1}{2}w \cdot \cos A - d \cdot \sin A}{1 - \sin A} \)

For the correct notch angle, \( 60^\circ \), the expression reduces to:

\[
r = \frac{\sqrt{3}w}{2} - d
\]

This expression was used to check \( r \) from measurements of \( w \) and \( d \).

**Accuracy:**
(a) If the notch angle differed by \( \pm 1^\circ \) from \( 60^\circ \), the calculated value of \( r \) would be in error by about \( \pm 0.0006" \).

(b) The estimated measuring error for \( d \) and \( w \) of \( \pm 0.00036" \) gives a maximum error in \( r \) of \( \pm 0.00067" \). The variation found in a batch of test-pieces was of this order, so it was considered that an average of the values calculated for \( r \) could fairly represent the actual value.
II. STANDARD PROCEDURE FOR CADMIUM PLATING (A.I.D. SPECIFICATION) *

1) Light rubbing of shank with fine wet emery paper.
2) Wiring up on copper wire.
3) Degreasing in I.C.I. Vapour Trichlorethylene Degreaser (10 secs.)
4) De-embrittlement Stoving (30 minutes at 400°F.)
5) Masking of heads by dipping in "liquid envelope green" varnish.
6) Drying of varnish 15 minutes minimum.
7) Electrolytic etch (200 a/ft²) 5 secs in 75% - 80% H₂SO₄.
8) 30 secs, rinse in water.
9) Electrolytic cleaning 10 secs, approx. 10% sodium cyanide.
10) 10 secs, approx. water rinse.
11) 25 mins. in Cd-plating bath (CdO + NaCN + small amount NaOH) at 8 to 9 a/ft² and 2 volts.
12) Water wash 15 secs.
13) 3 to 5 mins. immersion in 5% solution of sodium dichromate.
14) Final rinse cold water then hot water.
15) Final de-embrittlement stoving (4 hrs. at 400°F. (DTD 904)).

* At Industrial Plating & Research Company Limited, Trading Estate, Uxbridge, Middx.