

**AN INVESTIGATION OF THE EFFECTS OF HYDROGEN
ON THE BRITTLE FAILURE OF HIGH-STRENGTH STEELS**

EDWARD R. SLAUGHTER

E. ELLIS FLETCHER

ARTHUR R. ELSEA

GEORGE K. MANNING

BATTELLE MEMORIAL INSTITUTE

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FOREWORD

This report was prepared by the Battelle Memorial Institute under USAF Contract AF 33(616)-2103. The contract was initiated under Project No. 7351, "Metallic Materials", Task No. 73515, "Low Alloy Aircraft Steels", formerly RDO No. 591-80, "The Effects of Hydrogen on High Strength Steels", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with 1/Lt. Thierry N. Thys acting as project engineer.

This report covers period of work from July 1954 to June 1955.

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The effect of hydrogen on the delayed, brittle failure of high-strength steel was investigated by the use of room-temperature stress-rupture tests on unnotched, cathodically charged specimens. The principal variables in these tests were stress, strength level, structure, composition, and hydrogen content. The time for failure to occur decreased as the strength level of the steel or the applied stress was increased, but changes in structure or composition had little effect on the time to failure.

The martensite and bainite reactions were found to be unaffected by variations in hydrogen content.

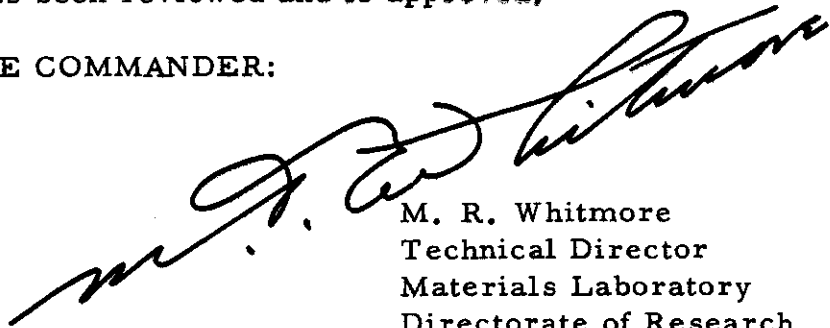
The diffusion of hydrogen through cathodically charged steel was investigated. In this study, stress was found to have no measurable effect on either the diffusion or the distribution of hydrogen in steel.

Hydrogen contents of steel cathodically charged under various conditions were determined.

PUBLICATION REVIEW

This report has been reviewed and is approved,

FOR THE COMMANDER:



M. R. Whitmore
Technical Director
Materials Laboratory
Directorate of Research

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AN INVESTIGATION OF THE EFFECTS OF HYDROGEN
ON THE BRITTLE FAILURE OF HIGH-STRENGTH STEELS

by

Edward R. Slaughter, E. Ellis Fletcher, Arthur R. Elsea,
and George K. Manning

INTRODUCTION

Structural failures have been encountered in certain aircraft parts made of high-strength steels when the applied stress was considerably lower than the nominal strength of the steel. In fact, it is characteristic of these failures that they occur while the part is subjected to a relatively low static load even though the same part previously may have withstood much higher dynamic loads. The fractures are brittle, but tensile specimens machined from the failed parts exhibit normal ductility and strength in the conventional tensile test. It is characteristic of these failures also, that the parts were exposed to processes during their manufacture which would introduce hydrogen into the steel.

The purpose of this investigation was to study the role of hydrogen in these delayed, brittle failures and to establish, if possible, the mechanism of the failures.

SUMMARY

This investigation has shown that delayed, brittle failures of high-strength steel can be caused by hydrogen. Such failures were obtained in SAE 4340 steel, heat treated to high strength levels, at stresses even less than 10 per cent of the nominal ultimate tensile strength. These brittle failures occurred in unnotched specimens when a critical combination of stress, hydrogen content, and time were exceeded. Consequently, it was concluded that a sustained uniaxial tensile stress is sufficient to cause a delayed, brittle failure in the presence of sufficient hydrogen.

The minimum stress necessary to cause failure was found to be related to the hydrogen content of the steel; it decreased as the hydrogen content increased. Both the minimum stress for failure and the delay were relatively unaffected by differences in the composition or structure of the steel. However, both the minimum stress and the time required to produce failure decreased as the nominal tensile strength of the steel was increased.

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With relatively high hydrogen contents in steels heat treated to high strength levels, delayed, brittle failures occurred in three stages when the critical combination of hydrogen content and stress were exceeded only slightly.

The first stage was the incubation period for the formation of a microscopic or a submicroscopic crack. This period was in excess of the time required to introduce hydrogen into the specimen and lasted as long as several hours.

The second stage was the propagation of a brittle crack during the period in which the stress exceeded the minimum stress, due to stress concentration at the crack front. The velocity of the brittle crack propagation in this period was in the order of inches per minute.

The third stage in the delayed, brittle failure was the sudden rupturing of the remaining section. This occurred when stress on the remaining section equaled or exceeded the notch-tensile strength. When the crack geometry was such that a portion of the remaining section was unrestrained, a ductile failure occurred in the third stage. Apparently, the third stage of fracturing was unaffected by the hydrogen content.

In a series of experiments in which the permeability of steel for hydrogen was measured, stress was found to have no measurable effect on the diffusion coefficient or on the solubility of hydrogen in steel.

Delayed, brittle failure was found to be inhibited at a temperature of -108 F for a period of more than 200 hours; while under similar conditions at room temperature, failure would have occurred within an hour.

Hydrogen was found to have no measurable effect on the temperature at which the martensite reaction began or on the temperature at which the reaction was essentially completed.

EFFECT OF HYDROGEN ON THE MARTENSITE REACTION

One possible explanation for the delayed-type brittle failures of high-strength steel suggests that hydrogen concentrates in the last remnants of austenite during hardening, and then retards the subsequent transformation of the hydrogen-rich austenite. Gamma iron has a considerably greater solubility for hydrogen than does alpha iron(1)*. Consequently, it seems likely that, as the austenite transforms to martensite, the hydrogen in the steel will tend to be rejected from the transformed material and will concentrate more and more in the remaining austenite. Thus, the last

*References appear at the end of the report.

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remnants of austenite may contain much more hydrogen than did the first austenite to transform. If the presence of hydrogen in the austenite extends the martensite reaction to lower temperatures, such hydrogen may promote the formation of microcracks. Hydrogen precipitating in these cracks then may produce high pressures which could fracture the steel.

Very little information was found in the technical literature regarding the effect of hydrogen on the transformations in steel, and none of this was related to the austenite-martensite reaction. Andrew, et al.⁽²⁾, showed that the isothermal transformation of a 3 per cent chromium steel was slightly slower at 1290 F in the presence of hydrogen; otherwise, there was no retarding effect. These authors indicated that hydrogen-treated steels seemed to expand less in transforming from gamma to alpha than did low-hydrogen steels. Perhaps hydrogen expands the austenite lattice. Smithells⁽³⁾ reported that the presence of hydrogen in iron increases the amount of heat generated in passing through the Ar₁, Ar₂, and Ar₃ points, and, in this respect, hydrogen has the same effect as metals in solution. Post, Lake, and Ham⁽⁴⁾ showed that the temperature of the gamma-alpha transition in iron is lowered slightly by the presence of hydrogen. Because no information related to the austenite-martensite reaction or to the austenite-bainite reaction at low temperatures was found, a study was made to establish the effect of hydrogen on the temperatures of the start and end of the martensite reaction in SAE 4340 steel.

The Greninger-Troiano quench-temper method was used to study the effects of hydrogen upon the temperature range of martensite formation. The experiments were performed as follows: Two specially prepared specimens with very low hydrogen contents were austenitized simultaneously in the same furnace for 30 minutes at 1550 F, one in a dry argon atmosphere and the other in wet hydrogen. The specimen treated with hydrogen during austenitizing picked up hydrogen and became a high-hydrogen specimen (about 3 ppm of hydrogen), whereas, the one heated in argon remained low in hydrogen (0.1 ppm or less, on the average). The two specimens were transferred quickly to a molten Wood's metal bath, which was at a selected temperature in or near the region where martensite forms, and were held for 30 seconds. The martensite formed at this temperature was tempered by heating to about 1080 F for 5 minutes in a lead pot, following which the specimens were water quenched to transform the remaining untransformed austenite to martensite. A metallographic comparison of the amounts of tempered martensite present in the two specimens showed the effect of this variation in hydrogen content on the amount of martensite formed. Pairs of specimens were transformed at various temperatures in the range from 633 to 186 F.

Commercial aircraft-quality SAE 4340 steel was obtained for this study. The certified analysis was as follows:

<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>
0.40	0.70	0.015	0.020	0.35	0.76	1.79	0.25

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The first requirement for the transformation studies was a stock of the SAE 4340 steel which contained as little hydrogen as possible. Because of the higher solubility of hydrogen in gamma iron, this requirement necessitated having a minimum of retained austenite. To obtain this, a bar of steel was austenitized at 1600 F for 1 hour. Then it was cooled to 1200 F and held at that temperature for 24 hours to insure complete transformation of the austenite to ferrite and pearlite. The technical literature indicates that transformation is essentially complete at this temperature in about 3-1/3 hours⁽⁵⁾. After the decarburized surface material had been removed, small specimens approximately 3/32 to 1/8 inch x 1/2 inch x 1 inch were cut from the steel. The specimens were then aged at 500 F for 24 hours to remove as much of the remaining hydrogen as possible.

Vacuum-fusion hydrogen analyses were performed on specimens of the low-hydrogen SAE 4340 steel after austenitizing under various conditions in dynamic atmospheres. For the sample size used, the sensitivity of the apparatus is ± 0.1 ppm of hydrogen by weight.

The analytical results indicated that the hydrogen-removing treatment and subsequent austenitizing in argon gave a hydrogen content in SAE 4340 steel of 0.1 ppm or less. This value is even lower than the constant residue of "nondiffusible" hydrogen of about 0.2 to 0.4 ppm by weight reported by Derge, Peifer, and Richards⁽⁶⁾ in their study of the loss of hydrogen from rail steels. Austenitizing in wet hydrogen resulted in a hydrogen content of about 3 ppm by weight, which is in the range of the solubility reported for iron and some steels at these temperatures.

Results of the metallographic studies of the specimens heat treated as described above to show the effect of hydrogen content upon the martensite reaction in SAE 4340 steel are summarized in Table 1. This steel was quite inhomogeneous, as shown by the severe banding of the microstructures. Because of this banding, it was difficult to estimate accurately the amount of tempered martensite in a given metallographic specimen. Therefore, estimates of the tempered martensite content of each specimen were made in these regions: (1) that band or portion of a band that showed the greatest amount of transformation (presumed to be the low-alloy band, as carbon and all of the alloy additions in this steel lower the temperature range for martensite formation), (2) that band or portion of a band that showed the least transformation (high-alloy band), and (3) the region of minimum banding. All three estimates for each sample are included in Table 1.

Comparison of the structures of the hydrogen-treated and argon-treated specimens quenched to a given temperature showed that hydrogen had little, if any, effect upon the martensite reaction in SAE 4340 steel. No difference was observed for specimens quenched to 633 F, the temperature at which martensite formation was just beginning in certain areas. Some pairs of specimens showed small differences in the amount of tempered martensite present. However, these slight differences were too small to be considered significant; undoubtedly they resulted from the inhomogeneities

TABLE 1. RESULTS OF THE METALLOGRAPHIC STUDY OF THE EFFECTS OF HYDROGEN CONTENT ON THE FORMATION OF MARTENSITE IN SAE 4340 STEEL

Specimen Number	Austenitizing Atmosphere ^(a)	Minimum Temperature of Martensite Formation, F	Estimated Tempered-Martensite Content, per cent		Region of Minimum Banding
			Low-Alloy Band ^(b)	High-Alloy Band ^(c)	
61A	Hydrogen	633	<1	0	Trace
61V	Hydrogen	633	<1	0	Trace
61H	Hydrogen	633	<1	0	Trace
62A	Argon	633	<1	0	Trace
62V	Argon	633	<1	0	Trace
62H	Argon	633	<1	0	Trace
3	Hydrogen	599	2	0	1
4	Argon	599	4	0	2
63A	Hydrogen	582	30-40	0	4
63V	Hydrogen	582	15	0	1
63H	Hydrogen	582	7	1/2	4
64A	Argon	580	20	0	<1
64V	Argon	580	1	0	<1
64H	Argon	580	7	0	<1
5	Hydrogen	556	50	5	35
6	Argon	556	50	0	35
59A	Hydrogen	551	55-60	0	40-45
59V	Hydrogen	551	50	0	40
60A	Argon	551	70-80	2	35
60V	Argon	551	70	3	40
49	Hydrogen	538	70	0-1	50
50	Argon	538	75	5	45
51	Hydrogen	534	70	30	55
52	Argon	534	80	20	60
7	Hydrogen	532	60-65	40	60
8	Argon	532	60	40-50	60
53	Hydrogen	530	80	15	55-60
54	Argon	530	80	0-3	50-55
9	Hydrogen	507	80	45	75
10	Argon	507	85	60	80
57	Hydrogen	502	95-97	70	90-93
58	Argon	502	95-97	70	90-93
11	Hydrogen	455	95-96	95-96	95-96
65	Hydrogen	455	99	99	99
12	Argon	455	>95	95	95
66	Argon	455	>99	98	>99

TABLE 1. (Continued)

Specimen Number	Austenitizing Atmosphere ^(a)	Minimum Temperature of Martensite Formation, F	Estimated Tempered-Martensite Content, per cent		Region of Minimum Banding
			Low-Alloy Band ^(b)	High-Alloy Band ^(c)	
13	Hydrogen	405	>99	>99	>99
14	Argon	405	>99	>99	>99
15	Hydrogen	355	100	100	100
16	Argon	355	100	100	100
17	Hydrogen	307	100	100	100
18	Argon	307	100	100	100

- (a) Low-hydrogen specimens austenitized in argon had hydrogen contents which averaged about 0.1 ppm by weight. Austenitizing in hydrogen produced hydrogen contents of approximately 3 ppm.
- (b) That band or portion of a band which showed the greatest amount of transformation observed.
- (c) That band or portion of a band which showed the least amount of transformation observed.

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in the steel. Thus, it was concluded that hydrogen had little, if any, effect on the M_s temperature of this steel.

However, as mentioned previously, it was expected that hydrogen, if it had any effect on martensite formation, would affect the end of the reaction more than the start, because of the hydrogen-concentrating effect during transformation. Metallographic examination of the "quench-temper" specimens initially cooled to temperatures in the range from 455 to 355 F showed no detectable differences which resulted from the hydrogen. Therefore, it was concluded also that hydrogen had little effect on the M_f temperature of this steel.

Thus, it has been shown that hydrogen content, in the range studied, had little, if any, effect on the temperature range of martensite formation or on the stability of austenite. Therefore, the suggestion that hydrogen may promote the formation of microcracks by extending the martensite reaction to lower temperatures, with hydrogen precipitating in these cracks producing high pressures and eventually fracturing the steel, is not the explanation of the delayed-type brittle failures.

BOLT TESTS

It might be expected that the composition of the steel would be a factor in the delayed-type brittle failures. In fact, a popular notion has held that SAE 4140 steel is much less susceptible to such failures than is SAE 4340 steel. Some have believed that such a behavior could be attributed to the reduced propensity of SAE 4140 steel for retaining austenite as compared with SAE 4340 steel. Therefore, the effects of composition on delayed, brittle failure were studied as a part of this investigation.

A series of experiments was performed in which bolts of SAE 4340, SAE TS4140, and SAE 1040 steels were charged with hydrogen and then subjected to a sustained load. Hot-rolled bar stock of these steels 1/2 inch in diameter was ground to 3/8 inch in diameter and threaded with 3/8-24 threads. These bolts were austenitized at 1550 F in a dry argon atmosphere and, after quenching, were tempered 1-1/2 hours at temperature to produce the desired hardnesses in these steels.

The bolts were charged with hydrogen by pickling or by cathodic charging and plating. The bolts were subsequently stressed by applying lubricated nuts with a measured torque, while the bolts were inserted in a steel block. Belleville spring washers under the nuts decreased the effect of any relaxation of the bolts and provided energy to propagate the fractures.

The conditions and results of these experiments are given in Table 2.

Continued

TABLE 2. EFFECT OF COMPOSITION ON THE DELAYED-FAILURE CHARACTERISTICS OF BOLTS

Processing	Specimen Identification	Steel SAE	Approximate Ultimate Tensile Strength, psi	Failure Attained	Approximate Time to Failure ^(a) , minutes
Stress with 50-ft-lb torque ^(d) (no pickling or plating)	Z-2	4340	230,000	No ^(e)	-
	B-9	1040	260,000	No	-
	C-2	4140	230,000	No	-
Pickle 3 minutes ^(b) , stress with 15-ft-lb torque	Z-6	4340	230,000	Yes	237+
	B-7	1040	260,000	Yes	14
	C-6	4140	230,000	No	-
Pickle 3 minutes ^(b) , cadmium plate ^(c) , stress with 20-ft-lb torque	Z-1	4340	230,000	Yes	45+
	B-1	1040	260,000	Yes	3
	C-1	4140	230,000	Yes	45+
	Z-3	4340	230,000	Yes	93+
	B-4	1040	260,000	Yes	2
	C-3	4140	230,000	Yes	70
	Z-4	4340	230,000	Yes	13+
	B-5	1040	260,000	No	-
	C-4	4140	230,000	Yes	13
	Z-7	4340	230,000	Yes	36+
	B-8	1040	260,000	Yes	5
	C-7	4140	230,000	Yes	20
Pickle 5 minutes, age at 185 F 6 minutes, pickle 2 minutes, cadmium plate, age 16 hours at room temperature, stress with 20-ft-lb torque	Z-5	4340	230,000	Yes	51
	B-6	1040	260,000	No	-
	C-5	4140	230,000	Yes	30
Pickle 12 minutes, stress with 20-ft-lb torque	Z-8	4340	230,000	Yes	118+
	B-10	1040	260,000	Yes	1/2
	C-8	4140	230,000	Yes	68+
	Z-13	4340	230,000	Yes	11
	B-15	1040	260,000	Yes	3
	C-13	4140	230,000	Yes	21
	Z-29	4340	230,000	Yes	106+
	B-29	1040	230,000	No	-
	C-29	4140	230,000	No	-
Pickle 12 minutes, age 1 minute at 180 F, stress with 20-ft-lb torque	Z-9	4340	230,000	Yes	20+
	B-11	1040	260,000	Yes	8+
	C-9	4340	230,000	Yes	25+
Pickle 12 minutes, age 3 minutes at 180 F, stress with 20-ft-lb torque	Z-12	4340	230,000	Yes	20+
	C-12	4140	230,000	Yes	48

Continued
TABLE 2. (Continued)

Processing	Specimen Identification	Steel SAE	Approximate Ultimate Tensile Strength, psi	Failure Attained	Approximate Time to Failure ^(a) , minutes
Pickle 12 minutes, age 5 minutes at 180 F, stress with 20-ft-lb torque	Z-10	4340	230,000	Yes	8+
	B-12	1040	260,000	(f)	-
	C-10	4140	230,000	Yes	118+
Pickle 12 minutes, age 10 minutes at 180 F, stress with 20-ft-lb torque	Z-11	4340	230,000	Yes	8+
	B-13	1040	260,000	No	-
	C-11	4140	230,000	No	-
Pickle 12 minutes, age 10 minutes at 180 F, stress with 20-ft-lb torque for 75 minutes, increase stress with 30-ft-lb torque	Z-14	4340	230,000	Yes	58
	B-16	1040	260,000	Yes	90
	C-14	4140	230,000	Yes	91
Pickle 12 minutes, age 20 minutes at 180 F, stress with 20-ft-lb torque for 75 minutes, increase stress with 30-ft-lb torque	Z-15	4340	230,000	Yes	100+
	B-17	1040	260,000	No	-
	C-15	4140	230,000	Yes	100+
Pickle 12 minutes, age 40 minutes at 180 F, stress with 20-ft-lb torque for 75 minutes, increase stress with 30-ft-lb torque	Z-16	4340	230,000	No	-
	B-18	1040	260,000	(f)	-
	C-16	4140	230,000	No	-
Pickle 12 minutes, age 80 minutes at 180 F, stress with 20-ft-lb torque for 75 minutes, increase stress with 30-ft-lb torque	Z-17	4340	230,000	Yes	100+
	B-19	1040	260,000	No	-
	C-17	4140	230,000	No	-
Stress with 30-ft-lb torque, preheat to 212 F, cathodically charge at 218 F in 7 per cent phosphoric acid with 5 drops per liter of catalytic poison	C-24	4140	230,000	Yes	3/4
Pickle 12 minutes, cool to -112 F and stress with 20-ft-lb torque, store at -112 F ^(g)	B-25	1040	230,000	Yes	4,548+
	C-25	4140	230,000	Yes	4,548+
Pickle 12 minutes, cool to -112 F, stress with 20-ft-lb torque, warm to room temperature in still air	Z-26	4340	230,000	Yes	139
	B-26	1040	230,000	Yes	136
	C-26	4140	230,000	Yes	99
Pickle 12 minutes, cool to -112 F and stress with 20-ft-lb torque, store at -112 F for 14,108 minutes (235 hours), warm to room temperature in still air ^(g)	Z-25	4340	230,000	Yes	14,160
Pickle 12 minutes, stress with 30-ft-lb torque and submerge in water at 163 F within 2 minutes	Z-27	4340	230,000	Yes	2.5
	B-27	1040	230,000	Yes	5.9
	C-27	4140	230,000	Yes	7.6

Footnotes appear on the following page.

Footnotes for Table 2

- (a) Origin of time was the time that loading was begun for precharged specimens, or the time at which cathodic charging was started for prestressed specimens. + indicates that failure was obtained but was not observed and that time was greater than time indicated.
- (b) All pickling was accomplished at room temperature in a 10 per cent by weight solution of hydrochloric acid in water. Reagent grade acid and distilled water were used.
- (c) All cadmium plating was accomplished in a cyanide bath for 20 minutes with current density of 0.1 ampere per square inch.
- (d) Loading was accomplished by applying lubricated nuts with a measured torque to bolt which had been inserted in a steel block.
- (e) As of June 7, 1955, all unfailed specimens have been stressed 427 days.
- (f) Specimens B-12 and B-18 were abandoned after 16 days without failure.
- (g) B-25, C-25, and Z-25 were stored in a container with dry ice over a holiday week-end. After the week-end, B-25 and C-25 were found broken and dry ice was almost exhausted. The specimens may have reached temperatures somewhat higher than -112 F.

Conrails

Typical delays to failure varied from about 2 minutes to approximately 4 hours. There were no qualitative differences in behavior among the steels, and typical delayed-type failures were obtained in all three steels. Consequently, these data support the conclusion that the mechanism of the delayed-type brittle failure is not influenced appreciably by changes in composition in the range of composition encountered in engineering alloy steels. However, there were indications that carbon steel required less aging to reduce significantly the detrimental effect of pickling. Several bolts of each steel were pickled simultaneously and then groups of one bolt from each steel were aged at 180 F for varying lengths of time to remove hydrogen. Delayed failure of carbon steel was eliminated by aging for approximately 10 to 20 minutes. However, one SAE 4340 bolt failed after having been aged 80 minutes at 180 F.

A potent effect of testing temperature also was observed. A bolt, cathodically charged at 218 F after stressing, failed within 45 seconds after the beginning of electrolysis. A bolt, pickled and cooled to -112 F before loading, was held in the stressed condition 235 hours at -112 F without failure. This bolt failed within an hour after being warmed to room temperature.

The effects of composition on delayed, brittle failures also were studied by means of room-temperature stress-rupture tests. The results of these tests will be described later in this report.

STRESS-RUPTURE TESTS DURING CATHODIC CHARGING

A characteristic feature of service failures of the delayed, brittle type is that the parts fail after sustaining a load for a considerable period of time. Usually the stresses involved at the time of failure were well below the yield point. Frequently, the parts withstood dynamic loads considerably greater than the load under which they subsequently failed. Therefore, it is necessary to consider the time element in studying such failures. The simplest loading system which would satisfy these requirements is a constant, sustained load. Therefore, a type of test which has been called a "room-temperature stress-rupture test" was the principal experimental tool used.

Frequently, the service failures have been associated with notches or with stress gradients which resulted from bending loads. Although the service stresses were usually complex, it would be important to an understanding of this phenomenon to determine whether such complex stresses are a necessary part of the delayed, brittle failures or were merely incidental. Therefore, an unnotched specimen loaded in tension was selected for the first studies. Uniaxial loading has the added advantage that the stresses may be analyzed more readily. Triaxiality of stresses will be treated as a separate variable.

Conclusions

It is well known that some, if not most, of the hydrogen contained in steel will escape at room temperature by diffusion in a matter of hours or days from a small specimen. This loss of hydrogen from a specimen would be a variable in a stress-rupture test in which the hydrogen was introduced prior to the test. The maintenance of a fixed concentration of hydrogen in a specimen would eliminate this variable and facilitate the study of the effects of other variables such as stress, composition, time, and strength level.

In the current work, the specimens were charged cathodically continuously under controlled conditions during the stress-rupture test. Thus, at the outset of the test, the hydrogen content of the specimens was continuously increasing. However, after steady-state conditions were attained, a constant hydrogen content would be maintained.

During electrolysis, hydrogen is liberated in the atomic form at the cathode surface where it either enters the steel or combines to escape to the atmosphere as molecular hydrogen. Only atomic hydrogen can be absorbed by the steel cathode. The "pressure" of atomic hydrogen at the cathode surface depends upon the conditions of electrolysis. According to Sims(7), the solubility of hydrogen in steel varies directly as the pressure of atomic hydrogen. Therefore, during the course of cathodic charging, the hydrogen content of steel would tend to approach an equilibrium value which is determined by the charging conditions.

The attempt to establish and maintain fixed concentrations of hydrogen in stress-rupture specimens was believed to be relatively successful. Experimental evidence to support this belief will be presented in the section entitled "Hydrogen Content as a Function of Cathodic Charging Conditions".

All of the stress-rupture test specimens with the exception of those used to study the effect of composition were from one heat of aircraft-quality SAE 4340 steel. A certified percentage analysis of this steel follows:

Composition, per cent							
<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>
0.40	0.77	0.015	0.022	0.28	0.80	1.78	0.22

This steel was purchased as 2-1/4-inch round, which was forged and rolled into 1/2-inch-diameter bars.

In order to obtain a uniform base material, a procedure was adopted to reduce the hydrogen content of the steel as much as possible. The steel was austenitized for one hour at 1550 F and furnace cooled to 1200 F. The temperature was maintained at 1200 F for 24 hours and then was lowered to 500 F for an additional 24 hours. The stress-rupture specimens were rough machined from material of this condition and then heat treated to produce the desired structure. Austenitization for all heat treatments was conducted in an atmosphere of dry argon. After heat treatment, the specimens were ground and the reduced sections were electropolished.

Contrails

The stress-rupture specimen is shown in Figure 1. The length of the reduced section was made large as compared to the diameter to reduce the effect of hydrogen diffusing from the reduced section into the larger sections which had a lower hydrogen content.

One of the static-loading devices used in the stress-rupture tests is shown in Figure 2. The load was measured by means of strain gages attached to a reduced section of the loading screw. Repeated calibrations of these devices at intervals for a period of one year agreed within ± 3 per cent. Belleville springs were provided to reduce the effect of any relaxation of the specimen or apparatus. There was generally a slight decrease in the indicated stress during the test, but this decrease was considerably less than the probable error in loading.

Continuous cathodic charging of the specimen was provided for by the electrolytic cell shown in Figure 2. The electrolyte was contained in a vessel of Pyrex tubing so that the specimen might be observed during the test. The bottom of the container was Hycar rubber, which formed a seal for the specimen. The reduced section and fillets of the specimen were the cathode, and the anode in the series of experiments in which Charging Condition A was used was a strip of antimonial lead. For Charging Condition A, the electrolyte used was a 4 per cent by weight solution of sulfuric acid in water to which was added 5 drops per liter of poison. This poison was composed of 2 grams of phosphorus dissolved in 40 milliliters of carbon disulfide. The current density used was 8 milliamperes per square inch. The currents were controlled manually and were subject to a variation of ± 10 per cent.

The procedure for the stress-rupture tests was as follows: The stress-rupture specimens, which were usually slightly tarnished following the electropolishing operations, were degreased in a proprietary alkaline cleaner, rinsed in distilled water, and dried in air. Specimens then were loaded statically and an electrical potential was applied before the addition of the electrolyte. Time, from the beginning of the electrolysis until total rupture, was measured either with a stop watch to the nearest second for short-time tests or with a running-time meter to the nearest one-tenth of an hour.

Effect of Stress

Variations in applied stress affected the time to rupture in a similar manner under a wide range of conditions of strength level, composition, structure, and, to a certain extent, hydrogen content. When other conditions were held constant, there were two ranges of stress which produced different effects on the time to rupture as is shown in Figure 3. In the higher range of stress, the time to rupture was relatively short and was only moderately affected by a change of stress. For example, as the stress was increased from 60,000 psi to 180,000 psi, the time to rupture decreased only from 20 minutes to 6 minutes for a steel heat treated to 230,000 psi

Contrails

Notes:

1. 0.333" diam and 0.256" diam to be ground after heat treatment concentric within 0.002" total indicator reading. Shoulders joining 0.030" fillet and $\frac{1}{2}$ " diam to be normal to axis.
2. 0.256" diam sections and fillets to be electropolished. Test section to be polished to 0.250" \pm 0.003" diam.
3. Tolerances $\pm \frac{1}{16}$ " except as noted.

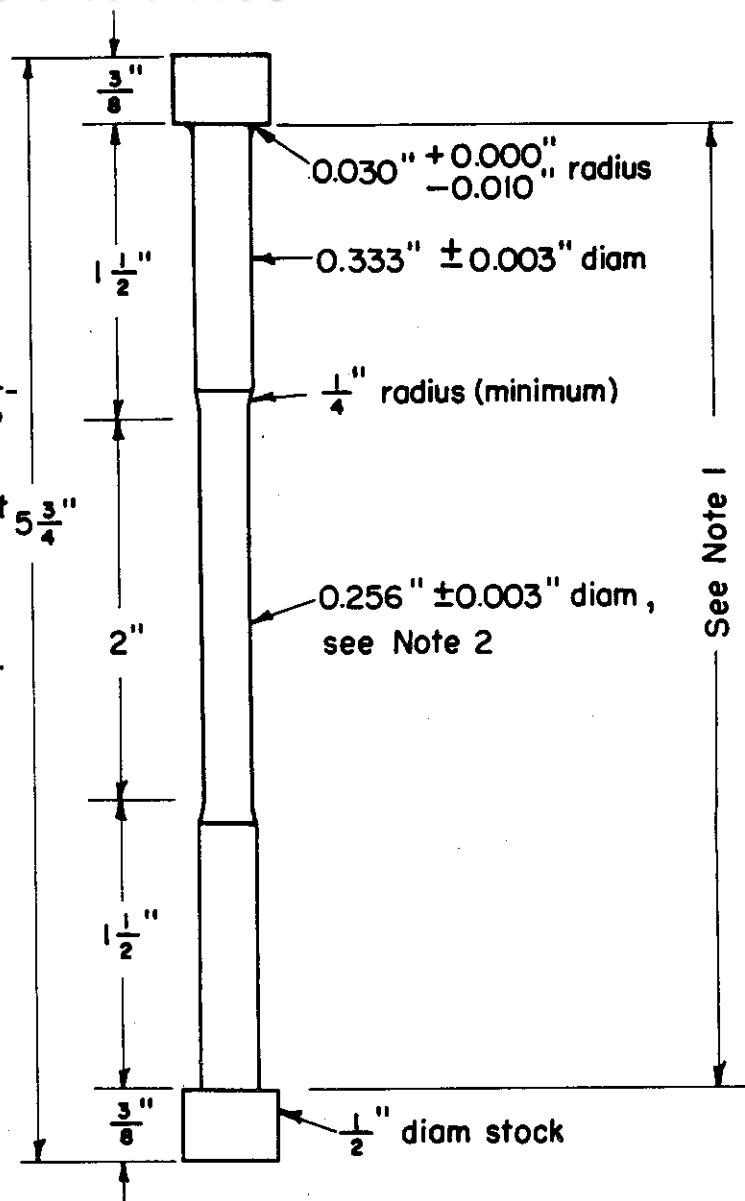


FIGURE 1. ROOM-TEMPERATURE STRESS-RUPTURE SPECIMEN

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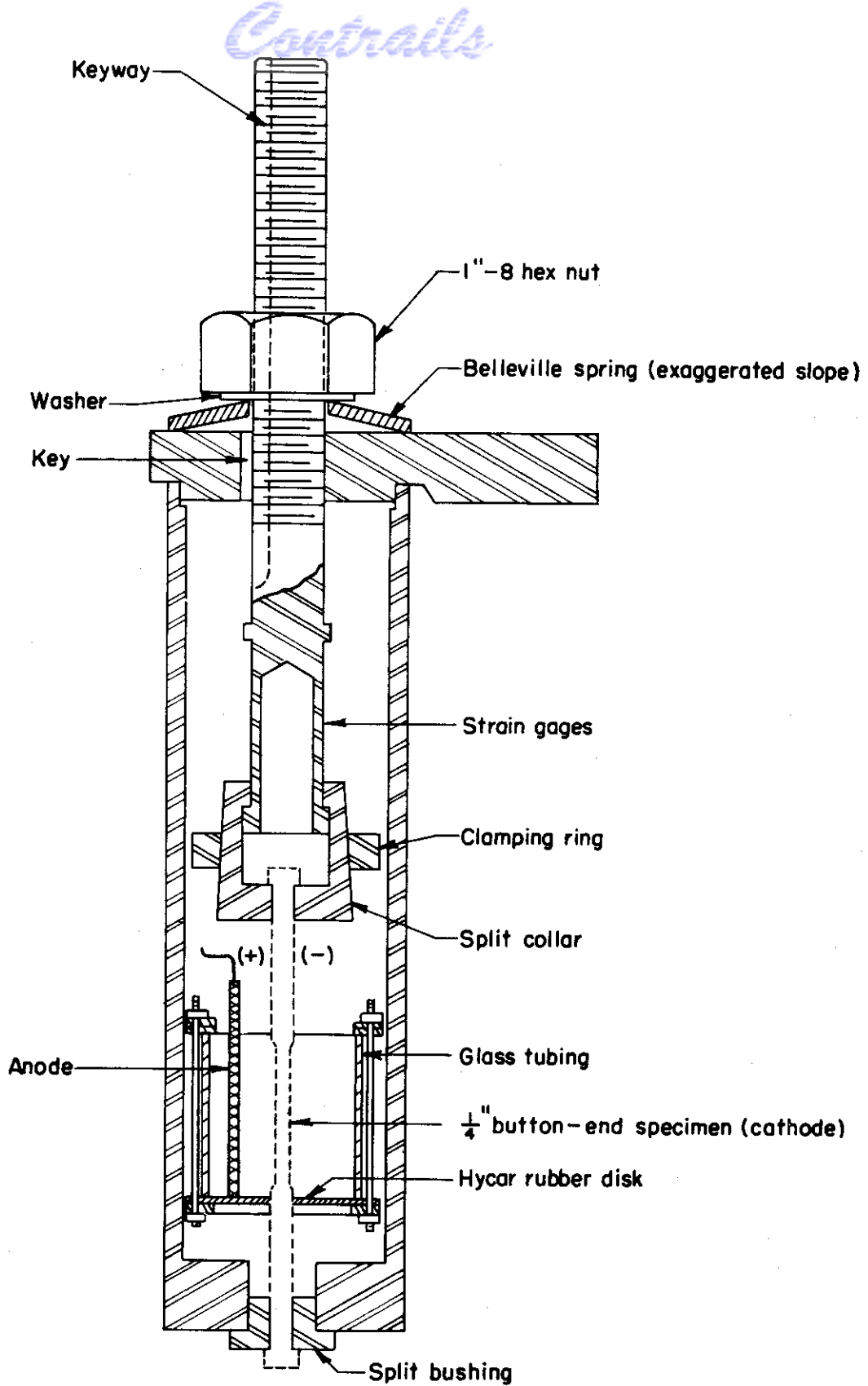


FIGURE 2. STATIC-LOADING DEVICE FOR 1/4-INCH BUTTON-END SPECIMENS

Electrolytic cell, for charging specimens with hydrogen while under stress, is shown in place.

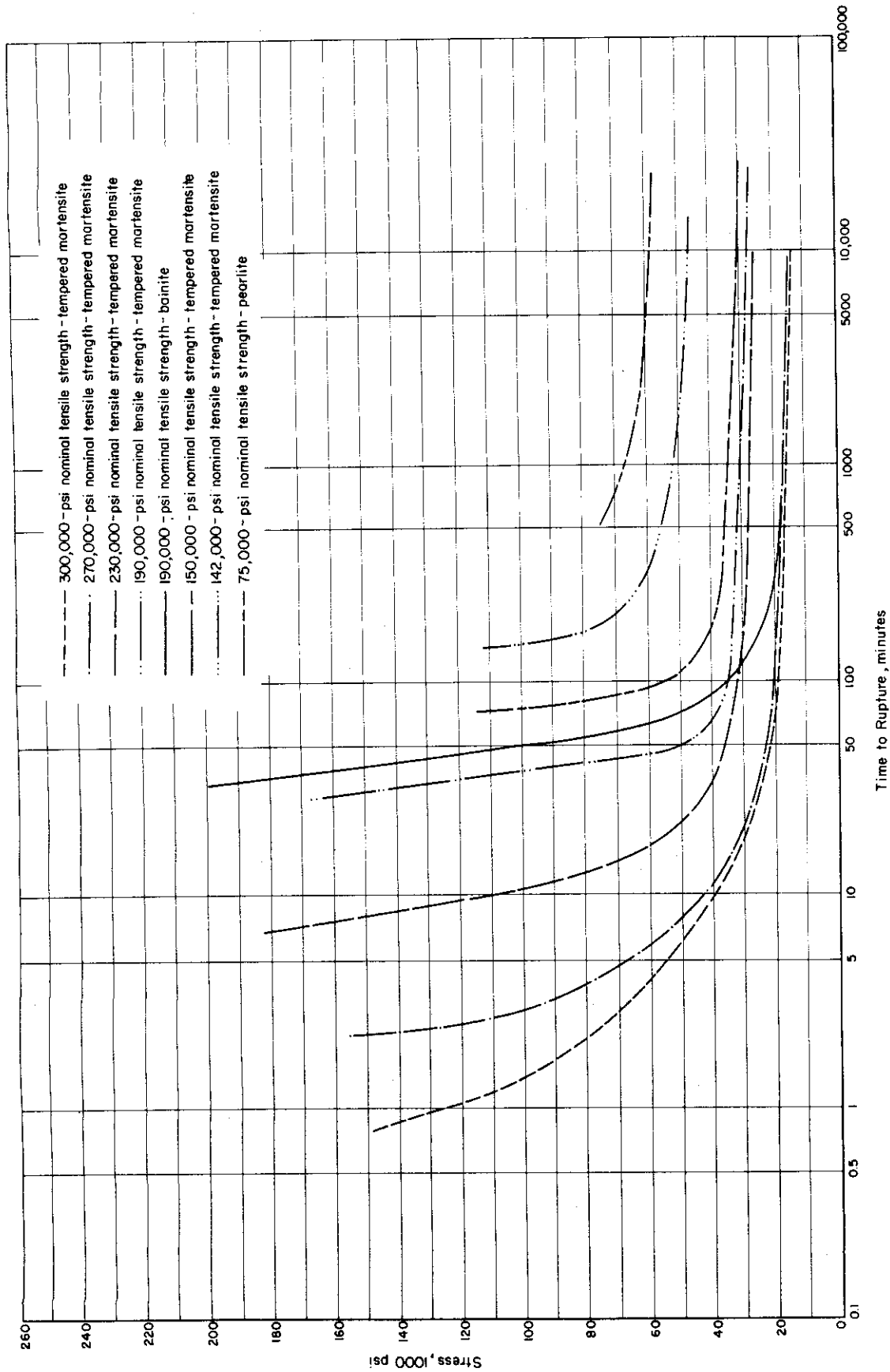


FIGURE 3. STRESS - RUPTURE CHARACTERISTICS OF AN SAE 4340 STEEL DURING CATHODIC CHARGING WITH HYDROGEN UNDER CONDITION A

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ultimate tensile strength and charged under Condition A. However, as will be discussed later in this report, in those specimens which failed after a relatively short time, the time to rupture probably was controlled more by the depth of hydrogen penetration than by the failure mechanism. In the lower range of stress, the time to rupture was longer by as much as a factor of 100. Time to rupture was greatly influenced by stress in this range; a slight decrease of stress resulted in a large increase in the time to rupture. For example, with conditions as in the previous example, with a decrease in the stress from 40,000 psi to 25,000 psi, the time to rupture increased from 40 minutes to approximately 10,000 minutes. Similar effects of stress were noted in the bend tests which will be discussed later.

Effect of Strength Level

The effect of strength level was studied with a group of SAE 4340 steel specimens in which the ultimate tensile strength varied from approximately 300,000 psi to 142,000 psi. All of these specimens were fully quenched to produce martensitic structures, and then tempered at temperatures in the range from 300 to 1200 F to produce variations in strength. The results of these studies are shown in Figures 3 and 4 and in Table 3. As the strength level was decreased from 300,000 psi to 142,000 psi, the time to rupture in the higher range of stress increased by a factor of approximately 100; the stress required to cause rupture in 10,000 minutes increased from 15,000 psi to 45,000 psi as the strength level was decreased in that range.

While the conditions of these tests would not be encountered in service, these tests demonstrate that hydrogen can cause steel to lose more than 90 per cent of its ability to withstand a sustained load in the case of steel heat treated to a high strength level. At the lowest strength level tested for the tempered martensite, the steel lost approximately two-thirds of its load-carrying ability.

Not only was the loss of strength greater as the strength level of the steel was increased, but also the duration of cathodic charging necessary for failure decreased as the strength level increased. This indicates that perhaps less hydrogen is required to produce a rupture in a steel of higher strength. On the basis of these experiments alone, delayed-type brittle failures would be expected to be an increasingly severe problem as the strength level of steel is increased.

It is of interest to note that rupture occurred in these tests with steels at a strength level as low as 140,000 psi, although service failures of this type have been restricted to steels having higher strength levels. This might logically be attributed to the fact that these tests are more severe with respect to the content of hydrogen than that experienced by service parts.

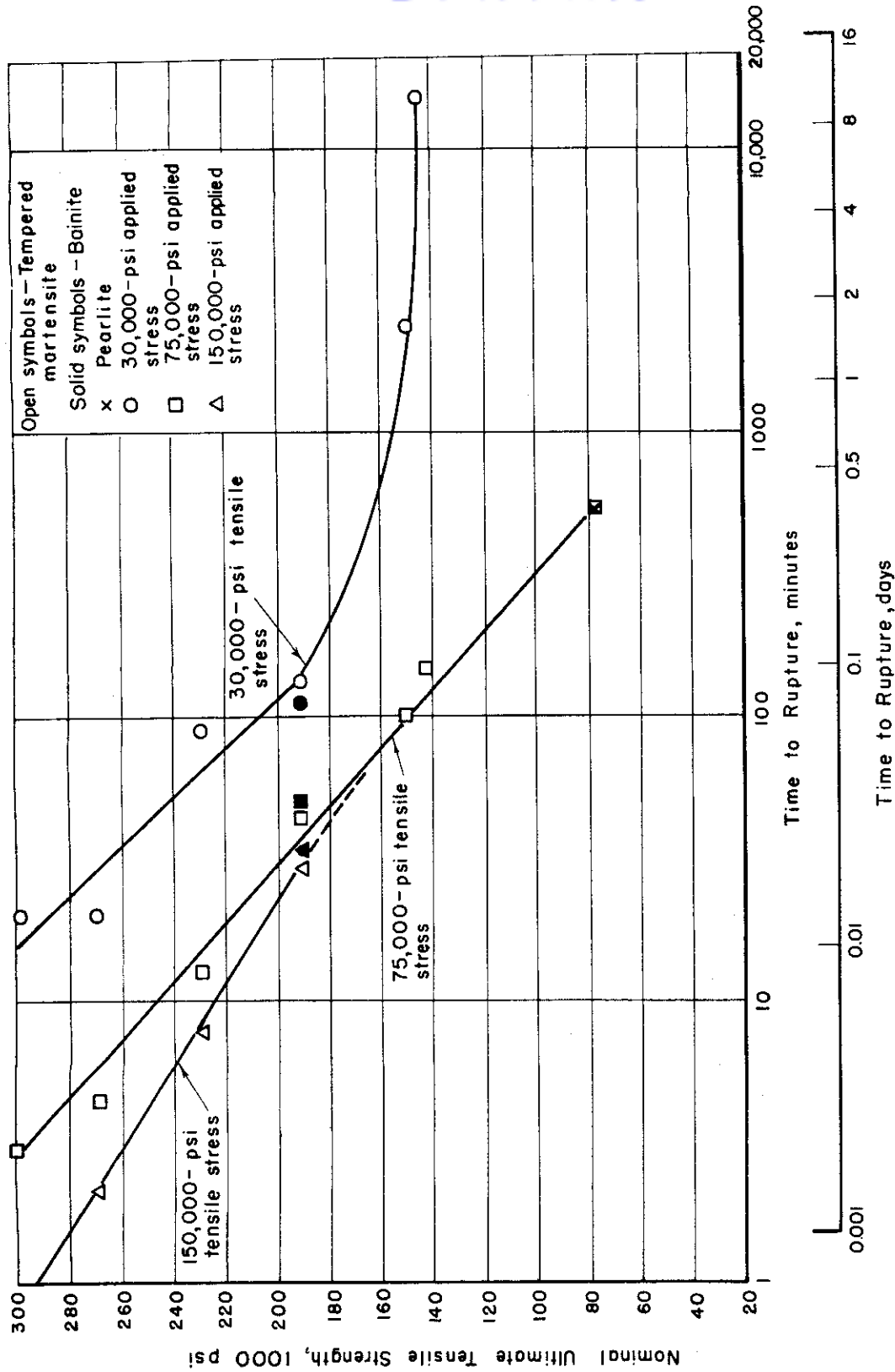


FIGURE 4. EFFECT OF NOMINAL STRENGTH OF AN SAE 4340 STEEL ON THE TIME TO RUPTURE DURING CATHODIC CHARGING WITH HYDROGEN UNDER CONDITION A WHILE UNDER STRESS

A-12391

Continued

TABLE 3. RESULTS OF ROOM-TEMPERATURE STRESS-RUPTURE TESTS OF UNNOTCHED SPECIMENS OF SAE 4340 STEEL CATHODICALLY CHARGED WITH HYDROGEN UNDER CONDITION A WHILE SUBJECTED TO STATIC TENSILE STRESS

Specimen	Stress, psi	Failure Attained	Time to Rupture ^(a) , minutes
<u>Nominal Tensile Strength 300,000 psi;</u> <u>Martensitic Structure</u>			
A105	150,000	Yes	0.75
A106	100,000	Yes	1.3
A107	30,000	Yes	26.8
A108	20,000	Yes	75
A109	15,000	No ^(c)	-
<u>Nominal Tensile Strength 270,000 psi;</u> <u>Martensitic Structure</u>			
A45	150,500	Yes	2.5
A48	100,000	Yes	2.8
A49	60,000	Yes	6.0
A40	39,000	Yes	13
A53	35,000	Yes	32.1
A41	30,400	Yes	19.2
A43	30,000	Yes	24.0
A47	20,000	Yes	492
A46	20,000	Yes	606
A42	20,000	No ^(d, e)	-
A52	15,000	Yes	72
A50	15,000	Yes	1458
<u>Nominal Tensile Strength 230,000 psi;</u> <u>Martensitic Structure</u>			
A68	175,000	Yes	6.9
A75	150,000	Yes	7.1
A31	102,000	Yes	14.5 ^(f)
A80	100,000	Yes	5.0
A27	100,000	Yes	12.3
A29	100,000	Yes	14.0 ^(f)
A70	50,000	Yes	16.6
A71	50,000	Yes	16.7
A72	50,000	Yes	16.7
A73	50,000	Yes	21.7
A32	47,500	Yes	22.6
A67	35,000	Yes	57.9
A61	32,000	Yes	382
A74	30,000	Yes	27.0
<u>Nominal Tensile Strength 230,000 psi;</u> <u>Martensitic Structure</u>			
A69	29,000	Yes	486
A77	25,000	Yes	128
A34	23,500	No ^(d)	-

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TABLE 3. (Continued)

Specimen	Stress, psi	Failure Attained	Time to Rupture ^(a) , minutes
<u>Nominal Tensile Strength 190,000 psi;</u> <u>Martensitic Structure</u>			
A 97	168,000	Yes	19.3
A 94	150,000	Yes	33.3
A 90	100,000	Yes	41
A 95	43,000	Yes	67
A 91	35,000	Yes	98
A 96	35,000	Yes	113
<u>Nominal Tensile Strength 150,000 psi;</u> <u>Martensitic Structure</u>			
A 88	100,000	Yes	86.5
A 85	45,000	Yes	142
A 82	35,000	Yes	309
A 87	30,000	Yes	169
A 84	30,000	Yes	2370
A 89	30,000	No ^(g)	-
A 83	25,000	Yes	4176
A 86	25,000	No ^(h)	-
<u>Nominal Tensile Strength 142,000 psi;</u> <u>Martensitic Structure</u>			
A 126	100,000	Yes	102
A 123	100,000	Yes	2940
A 125	75,000	Yes	246
A 127	50,000	Yes	3414
A 124	30,000	No ⁽ⁱ⁾	-
<u>Nominal Tensile Strength 190,000 psi;</u> <u>Bainitic Structure</u>			
A 115	189,000 ^(j)	Yes	23.1
A 111	150,000	Yes	51.5
A 112	100,000	Yes	46
A 113	30,000	Yes	114
A 114	25,000	Yes	192
A 116	20,000	Yes	312
<u>Nominal Tensile Strength 75,000 psi;</u> <u>Pearlitic Structure</u>			
A 98	75,000	Yes	516
A 100	71,000	Yes	630
A 102	70,000	Yes	978
A 101	64,000	Yes	1872
A 103	50,000	No ^(k)	-
A 99	50,000	No ^(l)	-

Footnotes appear on the following page.

Footnotes for Table 3.

- (a) Sulfuric acid electrolyte consisted of 4 per cent by weight of sulfuric acid in distilled water to which a solution of 2 grams of phosphorus in 40 milliliters of carbon disulfide was added. The phosphorus solution was added at the rate of 5 drops per liter of acid solution. Current density was 8 milliamperes per square inch.
- (b) Origin of time was at the addition of the electrolyte to the cell. Potential was applied to the cell before electrolyte addition.
- (c) Specimen A109 abandoned after 6000 minutes.
- (d) Test abandoned after 48 hours (2880 minutes).
- (e) Twenty minutes after end of cathodic-charging test, specimen was again loaded and failed with an increasing load at approximately 41,900-psi stress.
- (f) Load was released during electrolysis for 2 to 3 minutes and reapplied.
- (g) Specimen A89 abandoned after 18,516 minutes (12.9 days).
- (h) Specimen A86 abandoned after 18,546 minutes.
- (i) Specimen A124 abandoned after 14,340 minutes.
- (j) Specimen A115 "necked down" visibly, so that the true stress at the minimum section exceeded 189,000 psi.
- (k) Specimen A103 abandoned after 13,242 minutes.
- (l) Specimen A99 abandoned after 14,334 minutes.

The effect of structure on the loss of strength during cathodic charging was studied by comparing the loss of strength of specimens with a bainitic structure to the loss of strength of specimens with a martensitic structure of equal hardness. Specimens with bainitic structures were prepared by austenitizing at 1550 F in a dry argon atmosphere, quenching into a salt bath at 650 F, and then transferring the specimens to an air furnace at 650 F. Specimens were held at 650 F for 18 hours to insure completion of the transformation. The results of these stress-rupture tests under Charging Condition A are contained in Table 3 and Figures 3 and 4.

The effect of structure on the loss of strength during the stress-rupture tests also was studied with annealed specimens. However, it was not possible to obtain equal strengths with a tempered-martensite structure and an annealed structure. The annealed structure was obtained by isothermally transforming austenitized specimens at 1200 F for 24 hours. The results of these tests also are included in Table 1 and Figures 3 and 4.

Structure, per se, did not have a large effect on the stress-rupture behavior of steel during cathodic charging. As shown in Figures 3 and 4, specimens with a bainitic structure behaved much like the specimens with a martensitic structure of the same hardness. In the higher stress range, specimens with bainitic and martensitic structures showed almost identical behavior, but in the lower stress range, the bainitic structure was affected more adversely by the cathodic charging. As shown in Figure 4, extrapolation of the curve for the martensitic structure is consistent with the properties of the annealed structure.

Effect of Composition of the Steel

The bolt tests indicated that composition of the steel was not the controlling factor in these delayed-type brittle failures. However, the more precise room-temperature stress-rupture tests could give additional information as to any possible effect of composition. Therefore, stress-rupture tests using the standard cathodic charging conditions (Condition A) were conducted on specimens of SAE 4320 and a high-carbon steel as well as on SAE 4340. Preparation of the specimens and the test procedures were similar to those described earlier. Results of these tests are shown in Figures 5 and 6. The curves drawn on these figures are reproduced from Figure 3, while the plotted points are for the SAE 4320 or the high-carbon steel specimens.

The experimental points for the SAE 4320 and the high-carbon steel did not depart more from the curve for the SAE 4340 than did the individual test results for the SAE 4340 specimens. These results, and the results of

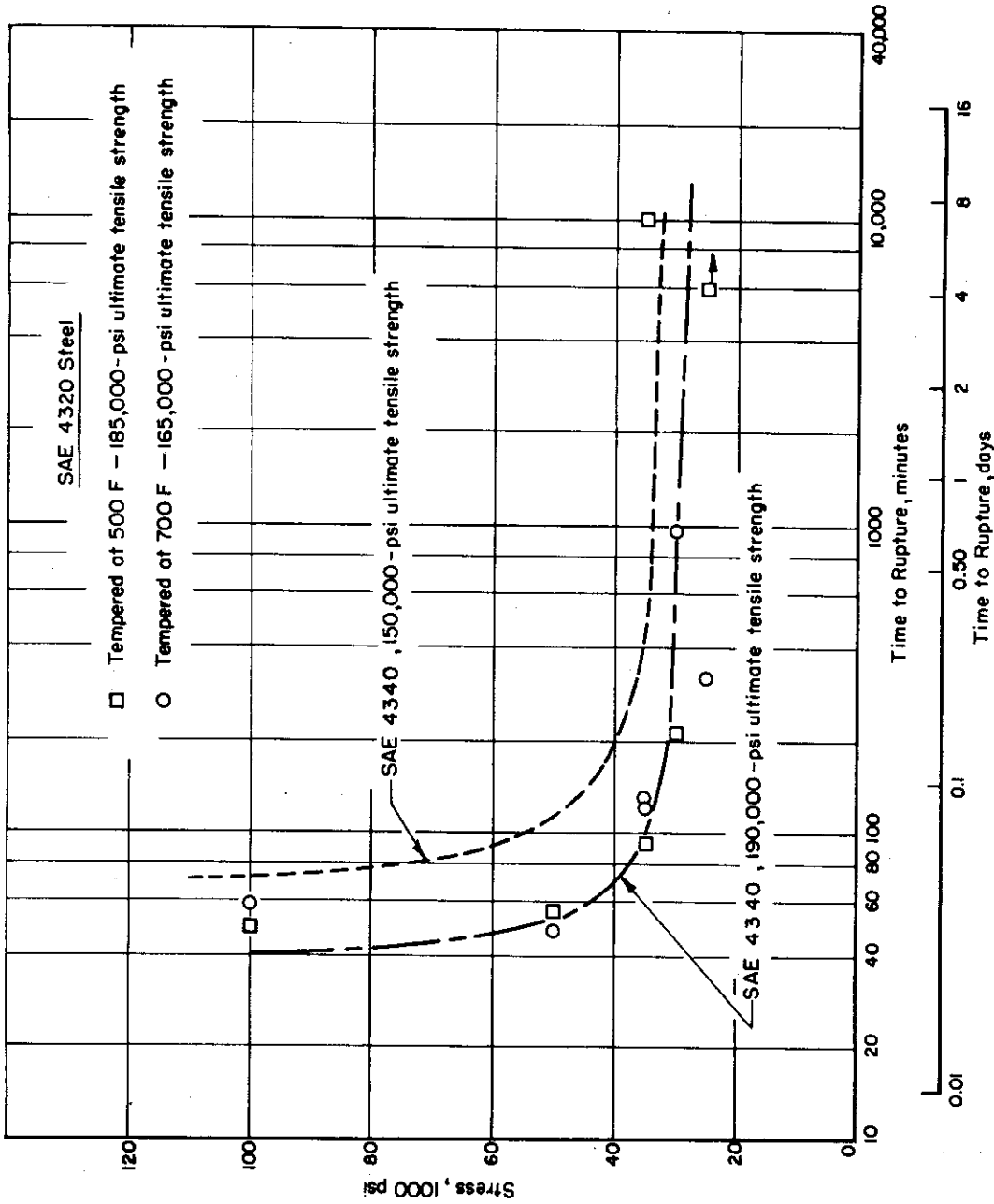


FIGURE 5. STRESS-RUPTURE CHARACTERISTICS OF AN SAE 4320 STEEL DURING CATHODIC CHARGING UNDER CONDITION A

Lines representing characteristics of SAE 4340 steel have been added for comparison.

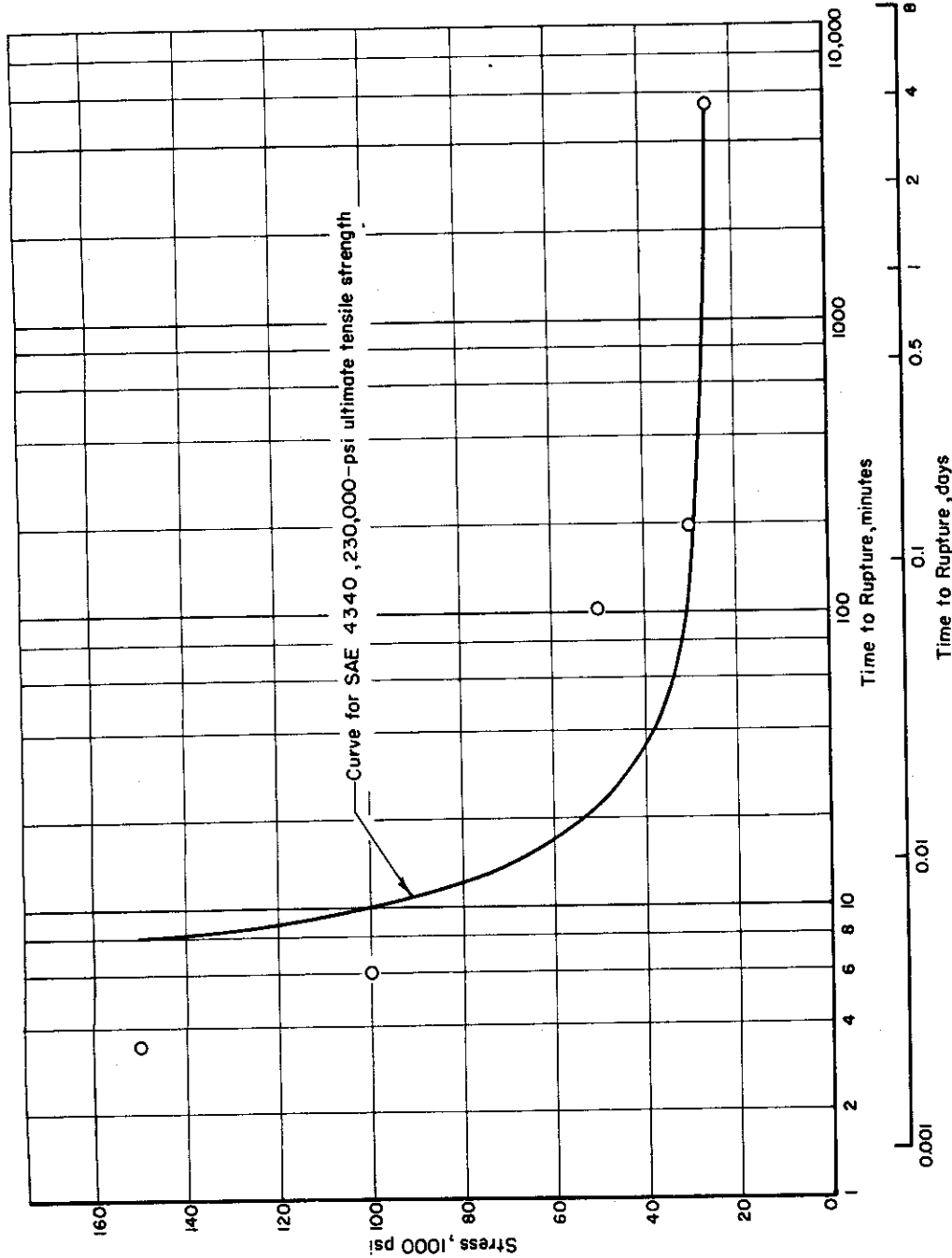


FIGURE 6. STRESS - RUPTURE CHARACTERISTICS, DURING CATHODIC CHARGING UNDER CONDITION A, OF A HIGH-CARBON STEEL HEAT TREATED TO HAVE AN ULTIMATE TENSILE STRENGTH OF 230,000 PSI

The characteristics of SAE 4340 steel at the same tensile strength have been added for comparison A-17631

bolt tests described previously, indicated that considerable changes in carbon content and in the common alloying elements had little effect on the delayed, brittle failure of these specimens under the conditions of testing. This small effect of compositions was in sharp contrast to the large effect of strength level on the loss of load-carrying ability in the presence of hydrogen during stress-rupture tests.

Effect of Section Size

In room-temperature, stress-rupture tests during cathodic charging, time to rupture must include some period which is required for hydrogen to diffuse to a sufficient depth to cause total rupture; that is, some if not most of the time required for rupture during these tests might be required for the absorption of hydrogen rather than for the growth of the crack. This period for the penetration of hydrogen should be sensitive to specimen size, decreasing with decreasing specimen size.

The time to rupture also must include some period for the propagation of a crack. It is reasonable to assume that this period, too, would decrease with decreasing section size. Therefore, as the section size is decreased, the times required for the absorption of hydrogen and for the growth of a crack would both diminish. Thus, in small specimens, any incubation period for the crack would become the important delay before rupture. In order to study this incubation period, a series of experiments was conducted with small specimens.

Bars of SAE 4340 steel 1/2 inch in diameter were hot swaged to 3/32-inch diameter and ground to 0.075-inch-diameter wire. These wires were heat treated to an ultimate tensile strength of 230,000 psi and were electropolished to produce diameters of either 0.065 or 0.030 inch. These small specimens were tested in stress-rupture tests with the standard charging conditions, Condition A. The results are shown in Figure 7, along with the curve which shows the results obtained for the 0.250-inch-diameter specimens.

At the higher range of stress, rupture occurred more rapidly as the section size decreased. That is, the incubation period for the crack was not the predominant part of the delay in the higher stress range. However, in the lower range of stress, the time to rupture became almost independent of specimen size as the stress approached the minimum stress for failure. The fact that the delay was independent of section size indicated that the incubation period became the predominant part of the delay.

This incubation period of a few hours was required with Charging Condition A, which produced a relatively high hydrogen content. It is possible that this period might be considerably increased with lower hydrogen contents such as might be present under service conditions. In

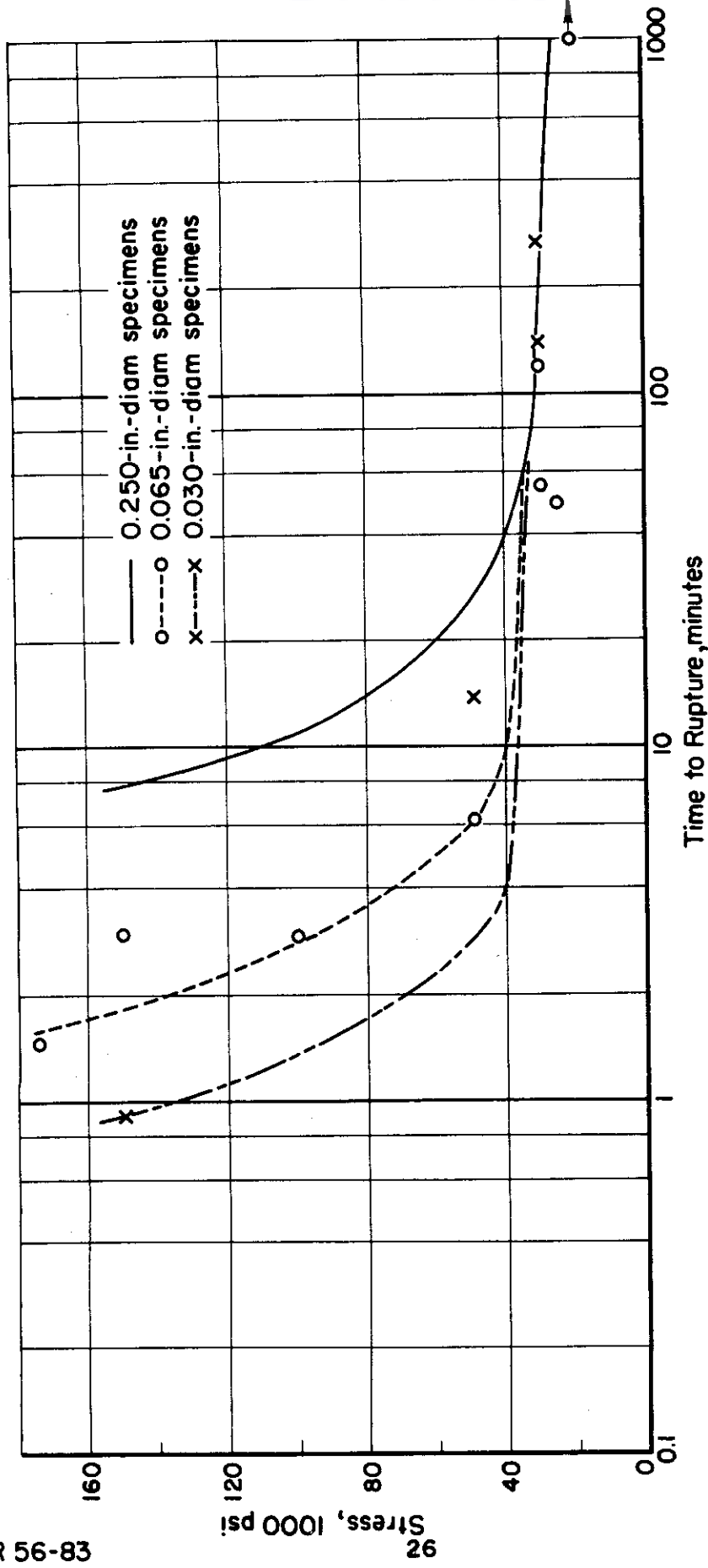


FIGURE 7. EFFECT OF SPECIMEN SIZE ON STRESS-RUPTURE CHARACTERISTICS OF AN SAE 4340 STEEL DURING CATHODIC CHARGING WITH HYDROGEN UNDER CONDITION A

A-14392

stress-rupture tests with 0.250-inch-diameter specimens, longer delays (up to 11.4 days) occurred with the milder charging conditions which resulted from charging in sodium hydroxide than with the more severe Condition A.

In these tests of long, small-diameter wire specimens, uniaxial stresses would have been approached very closely. A delay of several hours independent of the absorption of hydrogen was observed. These failures, therefore, contained all the essential features of the delayed-type brittle failures, and they were obtained with unnotched specimens. However, in a few preliminary stress-rupture experiments with 0.250-inch-diameter specimens, cathodically charged before but not during loading, delays before failure seemed to occur only with specimens which had been bent inadvertently during heat treatment so that the stresses were not uniaxial. Frohberg, Barnett, and Troiano⁽⁸⁾ obtained delayed failures at lower stresses with notched specimens than with smooth specimens. The results obtained in both these investigations indicate that triaxiality of stresses is a more severe condition than uniaxial stress for delayed, brittle failure.

Effect of Hydrogen Content

Cathodic charging with Condition A produced relatively high contents of hydrogen in the stress-rupture specimens. The present authors are not aware of any reliable data concerning the hydrogen content of steel components which have failed in a delayed, brittle manner in service. Nevertheless, it must be recognized that service parts almost certainly have lower hydrogen contents than those produced in the stress-rupture specimens using Charging Condition A.

Therefore, both stress-rupture tests and experiments involving the permeability of hydrogen through steel were employed to find cathodic charging conditions which would result in low hydrogen contents. The permeability experiments will be discussed in a later section. In the stress-rupture tests, it was assumed that, other conditions being constant, an increase in the minimum stress for failure would be the result of a lower hydrogen content. The validity of this assumption was verified later by hydrogen analyses on specimens cathodically charged in a manner similar to that used in the stress-rupture tests.

The hydrogen content of a cathodically charged steel decreased with decreasing current density. However, attempts to lower the hydrogen content of the specimens by decreasing the current density failed when the sulfuric acid electrolyte was used. The current density of 8 milliamperes per square inch used in Condition A approaches the limit of current density necessary to afford cathodic protection from chemical attack by the electrolyte. If cathodic protection were lost, pitting-type corrosion would

occur. This would reduce the cross section and introduce stress concentration. Also, the metal-acid reaction would result in varying and uncontrolled amounts of hydrogen being absorbed by the specimen.

It might be expected that cathodic protection would be obtained at lower current densities with weak acids than with strong acids. To investigate this, stress-rupture tests were conducted in which the electrolyte was composed of 10 per cent acetic acid, 45 per cent ethylene glycol, and 45 per cent water by volume and the current density was 1 milliamperere per square inch. This will be referred to as Charging Condition B.

The results of these experiments are shown in Figure 8. These results were similar to those obtained with the sulfuric acid electrolyte (Condition A), except that higher stresses and longer times were required to produce rupture. The minimum stress for failure was apparently between 60,000 and 75,000 psi, in contrast to the minimum stress for failure of about 25,000 psi with the sulfuric acid electrolyte. However, cathodic protection of the specimen was lost when the current density was reduced below 1 milliamperere per square inch for this electrolyte. Therefore, this series of experiments was abandoned without hydrogen analyses to confirm the presumably lower hydrogen content. However, data from the permeability experiments indicated that Charging Condition B produced an equilibrium hydrogen content approximately 1/3 of that produced by Charging Condition A.

Since it seemed unlikely that an acid solution could be found in which cathodic protection could be provided at much lower current densities, several other electrolytes were used in exploratory experiments. These electrolytes were either buffered solutions of weak acids or solutions of sodium hydroxide of various concentrations.

The procedure used in these experiments was modified somewhat from the procedure used with the sulfuric acid electrolyte. It was found that more consistent results could be obtained if the slight discoloration of the surface which resulted from the electropolishing operation was removed by polishing with 600X emery paper. It was noted also that the failures occurred preferentially at the ends of the cathodically charged area unless additional efforts were made to insure a uniform current distribution. Therefore, an anode was used which consisted of sixteen 30-gage platinum wires arrayed as elements of a cylinder concentric with the specimen. The concentration of the current at the ends of the cathodically charged area was greatly reduced by restraining the current by means of insulating collars to flow radially. The anode and restraining collars are shown in Figure 9.

The results of stress-rupture tests involving cathodic charging in 1/2 per cent sodium hydroxide solution at two current densities are given in Figure 10. Cathodic charging in 1/2 per cent sodium hydroxide at 125 milliampereres per square inch was Condition C; charging at 500 milliampereres per square inch, Condition D. It was noted that, as compared to the time to

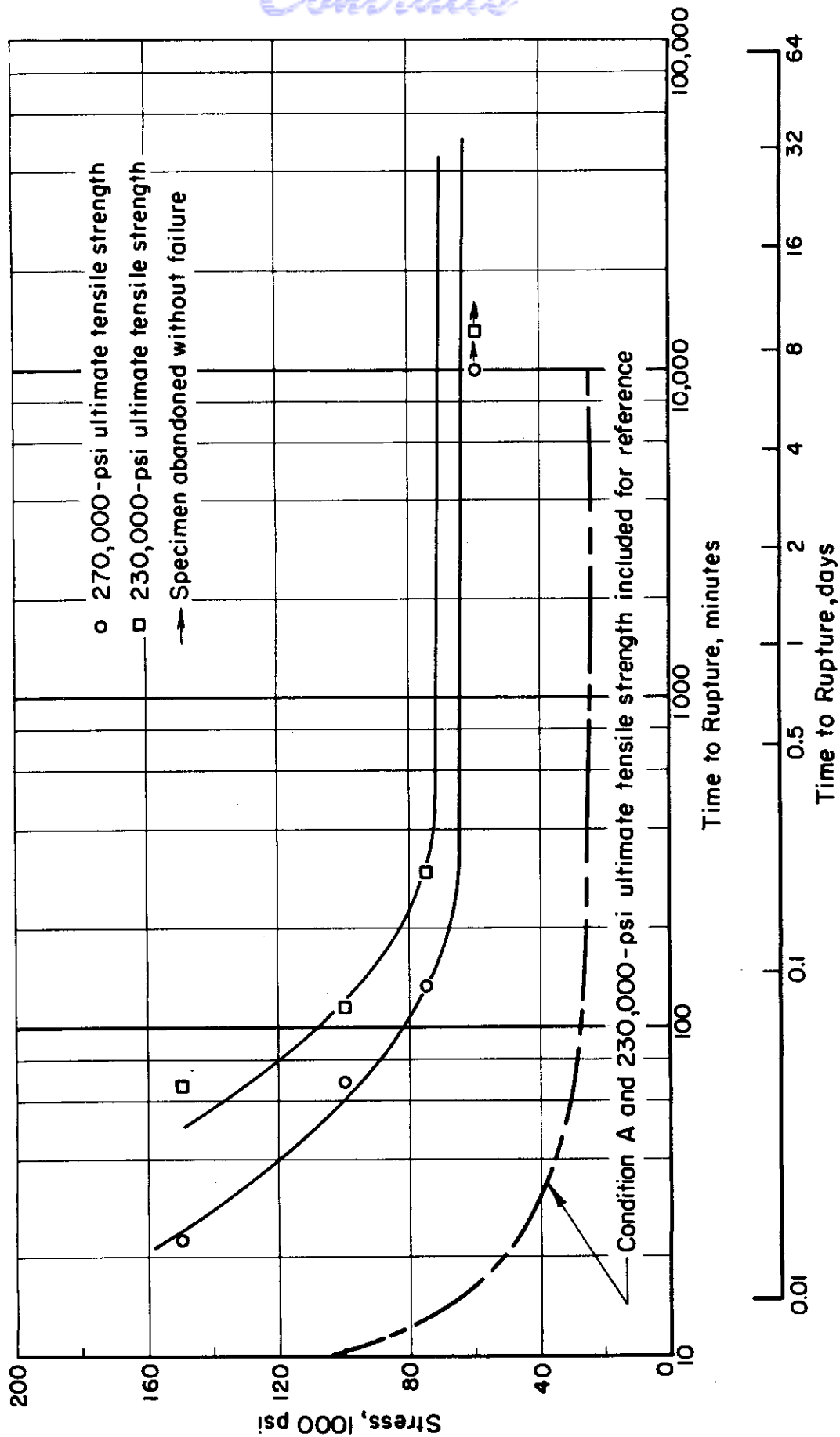


FIGURE 8. STRESS - RUPTURE CHARACTERISTICS OF AN SAE 4340 STEEL DURING CATHODIC CHARGING IN AN ACETIC ACID ELECTROLYTE AT 1 MILLIAMPERE PER SQUARE INCH

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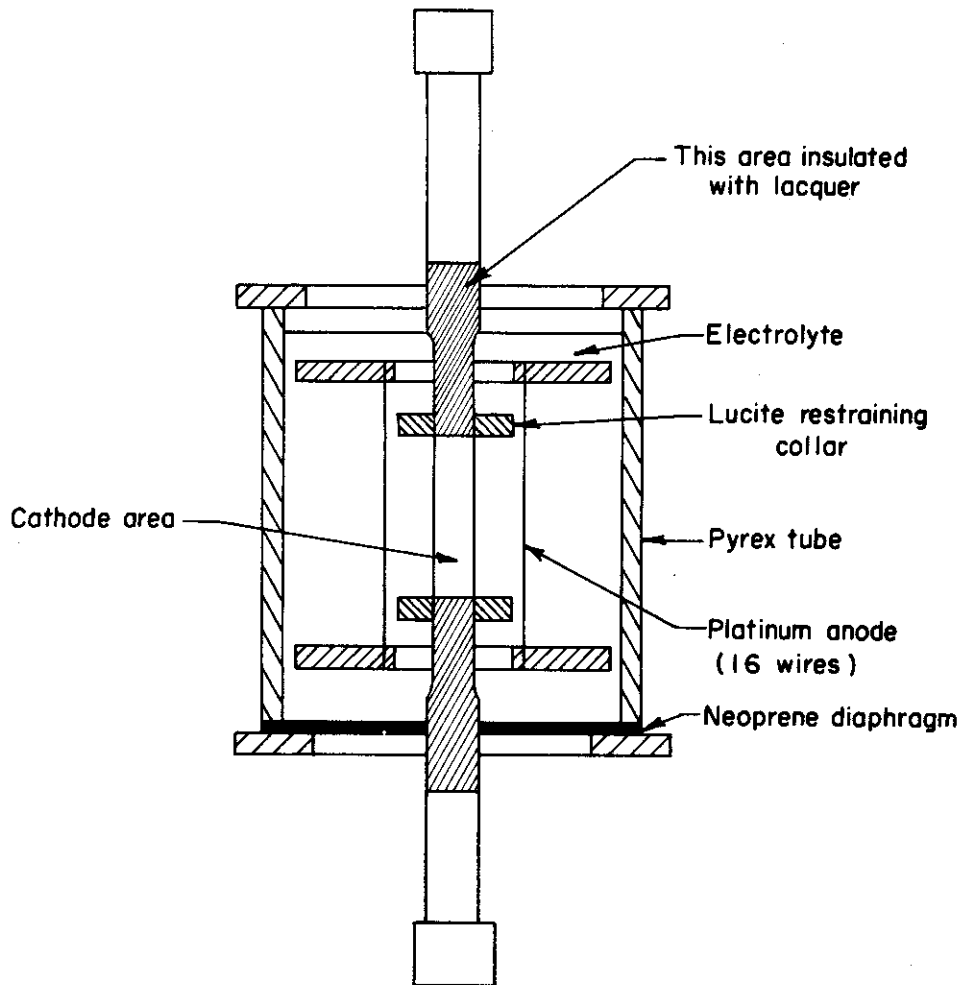
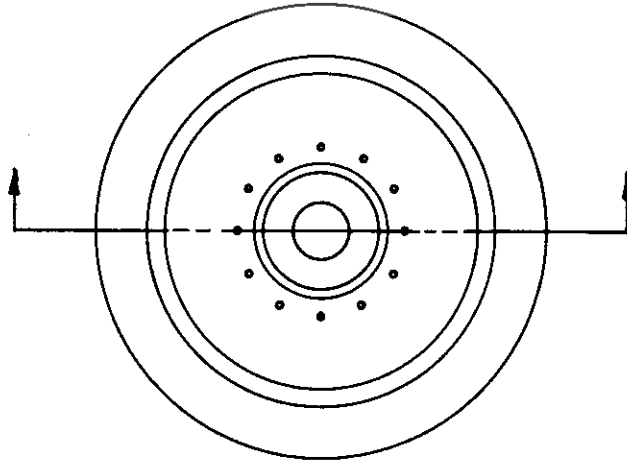


FIGURE 9. SCHEMATIC ARRANGEMENT OF THE ELECTROLYTIC CELL USED IN STRESS-RUPTURE TESTS INVOLVING CATHODIC CHARGING IN A SODIUM HYDROXIDE SOLUTION

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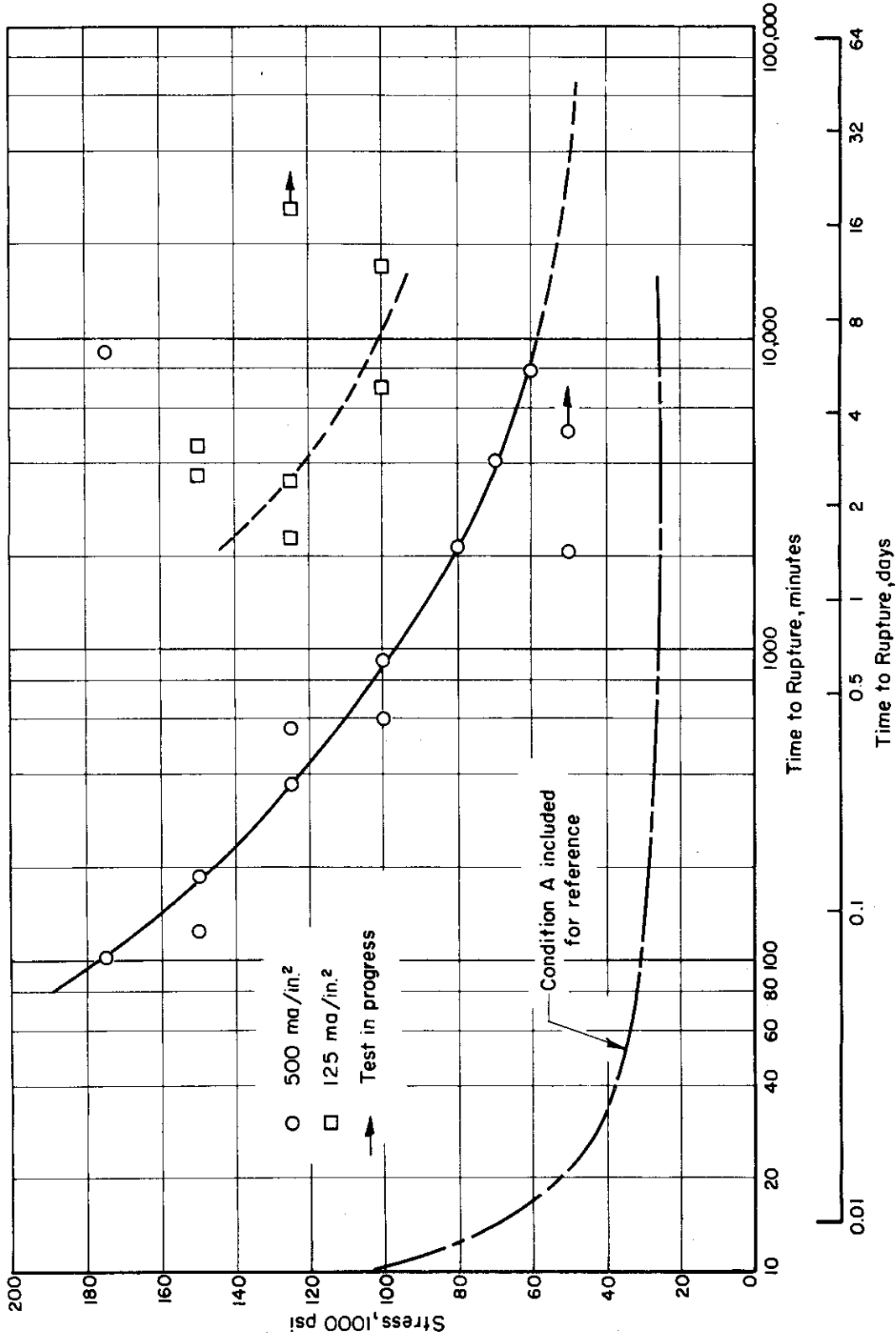


FIGURE 10. STRESS-RUPTURE CHARACTERISTICS OF AN SAE 4340 STEEL WITH AN ULTIMATE STRENGTH OF 230,000 PSI DURING CATHODIC CHARGING IN A 1/2 PER CENT SODIUM HYDROXIDE ELECTROLYTE

A-17630

rupture in the sulfuric acid electrolyte, the time to rupture in the sodium hydroxide electrolyte was greater by one order of magnitude for the higher current density and by about two orders of magnitude for the lower current density. One specimen, cathodically charged at 125 milliamperes per square inch and stressed at 100,000 psi, failed after 11.4 days; this was the longest delay for failure obtained in stress-rupture tests in which unnotched specimens were subjected to tensile loading. Although the minimum stress for failure has not been determined for these conditions, it appears likely that, in this range of current density, the minimum stress for failure is greatly influenced by current density.

The results of hydrogen analyses made on specimens charged under Conditions A, C, and D, to be described later, indicate that the minimum stress for failure was a function of the hydrogen content; the minimum stress for failure decreased with increasing hydrogen content.

Nature and Rate of Growth of the Fracture in Stress-Rupture Tests

In all of the previously described stress-rupture tests, the initial crack was normal to the principal tensile stress. This was demonstrated in stress-rupture tests in the higher stress range by the formation of a peculiar system of cracks. The formation and progress of these cracks at the surface could be observed readily, since numerous bubbles formed along these cracks. These cracks first became visible after 70 per cent or more of the total time to rupture had passed. These cracks grew in the form of a helix, sometimes a single crack would encircle the specimen 5 or 6 times. On a given specimen, these cracks formed a very uniform angle with a plane normal to the axis of the specimen. This deviation from a circumferential crack was established to be the result of a slight torque transmitted from the loading screw. Failure occurred in a direction normal to the resultant of the axial tensile stress and the small, tensile component of the torque. However, this torque was not sufficient to affect the magnitude of the principal stress appreciably, for the resultant tensile stresses made angles of from only 0 to 3 degrees with the specimen axis.

Very little elongation occurred as these cracks formed. The appearance of the first few cracks usually was accompanied by a drop in the load, which was estimated to be the result of an elongation of the specimen in the order of 0.00005 inch.

These cracks grew much more rapidly in the circumferential direction than in the radial direction, since they were many times as long as they were deep. That is, the cracks grew much more rapidly at the surface, where a high concentration of hydrogen existed, than they did within the specimen, where the concentration of hydrogen was much lower. The linear velocity of crack propagation at the surface was estimated to be $3/4$

of an inch per minute in one instance. Visible evidence of these cracks was not observed prior to rupture in the lower range of stress, although in some tests the specimen had been examined within two minutes of failure.

Total rupture of the specimens occurred when the stress on the remaining section approached the notch tensile strength. For example, stress on the remaining section of a specimen with an ultimate tensile strength of 230,000 psi was 338,000 psi when computed as the ratio of load to area remaining just prior to fracture. The area used in computing this stress was the area remaining below the bottom of one of these well-developed helical cracks adjacent to the fracture. It is believed that this final rupture of the specimen is unaffected by the hydrogen content. In stress-rupture tests in the lower stress range where the hydrogen-induced fracture apparently started at a single point and progressed radially, there was a ductile fracture around the remaining portion of the circumference. Thus, there were ductile failures in the regions of the highest concentration of hydrogen, but only where failure had occurred at very high strain rates.

Differences Between Delayed, Brittle Failures and Hydrogen Embrittlement

At this point, it is convenient to consider the differences which exist between hydrogen embrittlement and the delayed, brittle failure of steel caused by hydrogen. While these two effects may be related, the present investigators believe that they are not identical.

Numerous investigators have observed that a loss of ductility results from the presence of hydrogen in ferritic steel particularly at low strain rates. This loss of ductility generally has been termed "hydrogen embrittlement". An attempt will be made to show that a loss of ductility, as determined by the most precise methods available today, is not necessarily involved in delayed, brittle failure. The results of certain stress-rupture tests best show the differences between hydrogen embrittlement and delayed, brittle failure.

The stress-rupture tests to be considered are those conducted at, say, 50,000 psi and on a steel of intermediate strength level, for example, 190,000 psi ultimate tensile strength. Muir, Averbach, and Cohen⁽⁹⁾ determined the elastic limit of hardened carbon steel with methods capable of detecting a residual strain of 2×10^{-6} . An elastic limit of very close to 100,000 psi was obtained for a 0.41 per cent carbon steel with an ultimate tensile strength of 190,000 psi. It is apparent then that, if any permanent deformation occurred in the stress-rupture tests under consideration (50,000 psi stress and 190,000 psi ultimate strength), the amount of deformation was extremely small (less than 2×10^{-6}). The elastic strain at 50,000 psi was 850 times the limit of plastic deformation detectable by Muir, Averbach, and Cohen. Therefore, the present investigators believe that the

loss of the ability to plastically deform a measurable amount under these conditions could not account for the observed results, for failures were obtained in stress-rupture tests under these conditions.

Within the elastic range, a brittle and a ductile material are indistinguishable. The plastic deformation which distinguishes a ductile material from a brittle material occurs only above the elastic limit. Therefore, ductility would be a factor in these tests only if the stress were increased above the elastic limit, or if the elastic limit of the specimens were lowered greatly by the presence of hydrogen. However, several investigators have shown that hydrogen does not alter the stress-strain relationship prior to fracture in a conventional tensile test. Thus, it seems unlikely that hydrogen has any large effect on the elastic limit. Therefore, the stress exceeded the elastic limit in these tests only after a crack had been formed and had grown to an appreciable size. Obviously the conditions during the formation of the crack are the conditions of most interest.

Consequently, it can be concluded that measurable plastic flow, which is necessary to reveal hydrogen embrittlement, is not a factor in the initial stages of delayed, brittle failure.

From the preceding considerations, a role of hydrogen in delayed, brittle failure is suggested. Through some time-dependent process, probably involving diffusion, the action of a critical combination of hydrogen content and stress lowers the cohesive strength of the steel to the level of the applied stress, initiating a fracture. A possible explanation for this loss of cohesive strength is as follows: Hydrogen, interacting with lattice imperfections and dislocations arrayed on crystallographic planes normal to the principal tensile stress, increases the interatomic spacing across these planes, thereby lowering the cohesive strength. Elastic expansion of the lattice, as a result of the applied tensile stress, enables the hydrogen atoms to concentrate in these planes. It should be pointed out that, although a ductile material such as steel may have a fairly definite cohesive strength, ordinarily it cannot be measured because failure is preceded by slip. By definition, cohesive strength is the maximum stress required to cause tensile fracture in the absence of any deformation in an unnotched bar.

BEND TESTS

It might be argued that action of the electrolyte at the specimen surface influenced the failures in the stress-rupture tests. Any surface effect of the electrolyte was eliminated in a series of experiments in which specimens statically loaded in bending were charged cathodically on the compression side. These tests also were useful in determining whether delayed failures are dependent upon the hydrogen content or upon the total quantity of hydrogen which traverses a given region by diffusion.

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The specimens used in this series of experiments were bars of aircraft-quality SAE 4340 steel, 1/2 inch thick by 1-1/2 inches wide by 8 inches long. Some of these bars were from the heat of steel described in the section on "Stress-Rupture Tests", while other specimens were from another heat of aircraft-quality SAE 4340, having the following certified percentage analysis:

Composition, per cent							
<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>
0.39	0.76	0.017	0.021	0.27	1.75	0.86	0.22

These specimens were processed to eliminate hydrogen and heat treated in a manner similar to that used for the stress-rupture specimens. All of these specimens were heat treated to an ultimate tensile strength of approximately 230,000 psi.

An electrolytic cell was cemented to one side of each specimen with a portion of that side exposed as the cathode, as shown in Figure 11. A static bending moment was applied to the specimen so that the side to which the cell was attached was stressed in compression. The opposite side of the bend specimen was exposed to the atmosphere and was stressed in tension. The tension surfaces of the specimens were notched with transverse slots cut by a 0.020-inch-thick abrasive cut-off wheel. The depth of these slots was varied so that the thickness of the specimens at the base of the notch varied from 0.075 inch to 0.250 inch. The stress on the specimen was computed as the stress at the base of the notch, neglecting the effects of stress concentration. That is, the stresses were computed by the elastic theory for a section equal to the section at the base of the notch, which was subjected to the applied bending moment.

These specimens were cathodically charged in a 4 per cent sulfuric acid electrolyte with added poison at a current density of approximately 33 milliamperes per square inch. A hydrogen gradient was established through the specimen with the hydrogen content being highest at the cathodically charged surface and lowest at the opposite surface where hydrogen was escaping to the atmosphere. Thus, in the region of highest hydrogen content, compressive stresses existed. Along the neutral axis of this specimen, an intermediate hydrogen content was obtained, while at the surface stressed highly in tension, a low concentration of hydrogen was obtained.

Delayed fractures were obtained, but none of them originated at the cathodically charged surface. The region near the cathodically charged surface behaved in a ductile manner.

As in the tensile tests, the time to rupture increased as the stress was decreased to 80,000 psi. This is shown in Figure 12. One specimen failed after a delay of 15 days, which is the longest delay before failure yet obtained in the Battelle investigation. Since this specimen was only

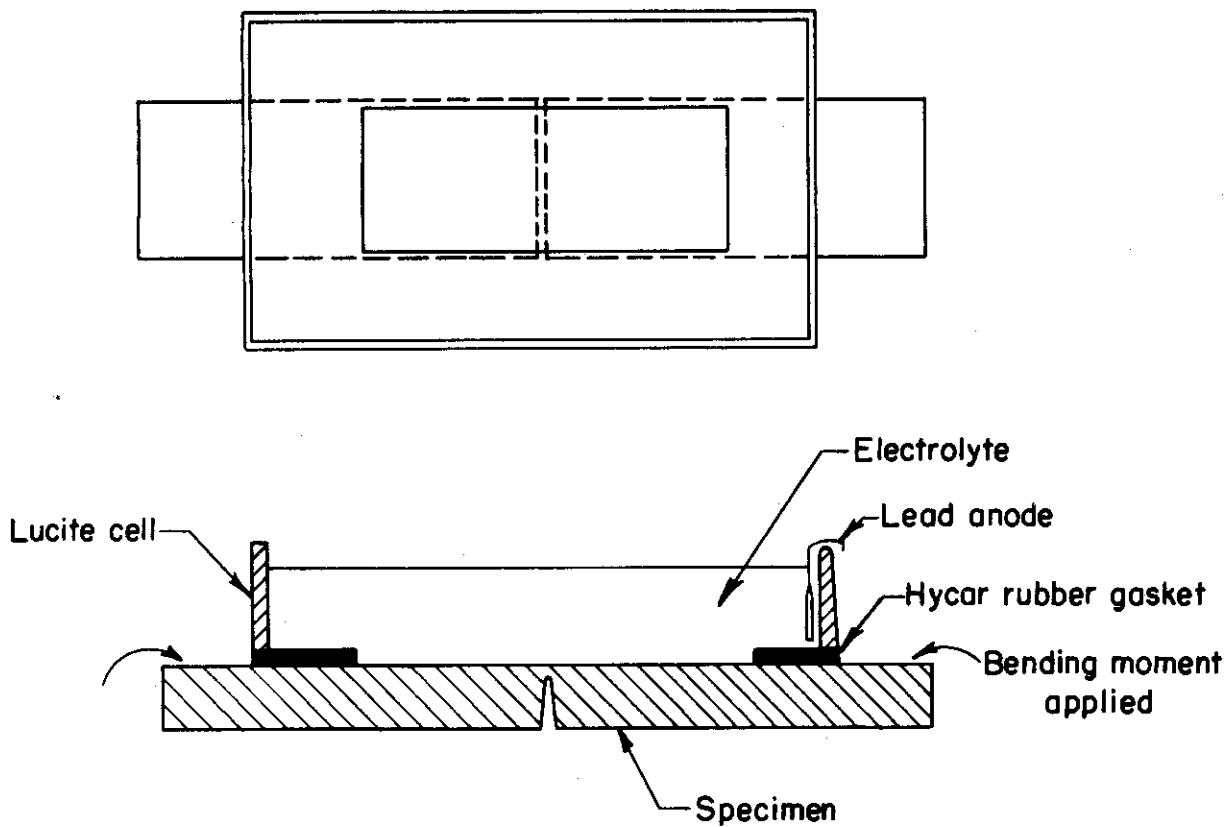


FIGURE II. SCHEMATIC ARRANGEMENT OF THE ELECTROLYTIC CELL AND SPECIMEN USED IN THE BEND TESTS

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0.075 inch thick at the minimum section, the steady-state concentration gradient of hydrogen should have been obtained in approximately 400 minutes; therefore, the period for establishing the necessary content of hydrogen within the specimen would be a very small portion of the 15-day delay.

These data indicated that an unlimited amount of hydrogen can traverse a region by diffusion without producing rupture, provided that a critical combination of hydrogen content and stress is not exceeded. For example, a bend specimen was charged cathodically for 43 days without rupture, while the surface from which the hydrogen was escaping was stressed to 80,000 psi. At this stress level, and at charging conditions to produce a high content of hydrogen, a stress-rupture specimen failed in about 15 minutes. In the 43-day period, much more hydrogen diffused through the bend specimen than could have been absorbed by a tensile specimen in 15 minutes. This series of experiments gave results which support the conclusion obtained from the stress-rupture tests that the minimum stress for failure increased with decreasing hydrogen content.

When the stress exceeded 100,000 psi, which corresponded to the upper range of stress in the stress-rupture tests, the time to rupture increased approximately as the square of the thickness. This is shown by Figure 13 in which the abscissas are rupture times divided by the squares of the specimen thickness. For a given stress in this range, the abscissas for the specimens with different thicknesses tend to have about the same value. This relationship between time and square of the thickness was consistent with the assumption that nearly all the time to failure was required to establish some minimum content of hydrogen less than the steady-state content of hydrogen at some distance from the cathodically charged surface, this distance being proportional to the thickness. This indicated that nearly all of the time was required to establish that content of hydrogen in the region where a certain tensile stress existed. The data also indicated that failure did not occur until a certain combination of hydrogen content and stress had been exceeded.

PERMEABILITY TESTS

The effect of stress on the distribution of hydrogen in steel was studied by means of experiments in which the permeability of steel for hydrogen was measured under various conditions. Similar experiments also were used to study the effect of cathodic charging conditions on the equilibrium hydrogen content in steel.

The specimens used in these experiments were made of SAE 4340 steel heat treated to 195,000 psi ultimate tensile strength. The specimens were tubular tensile specimens 3-1/2 inches long and with an inside

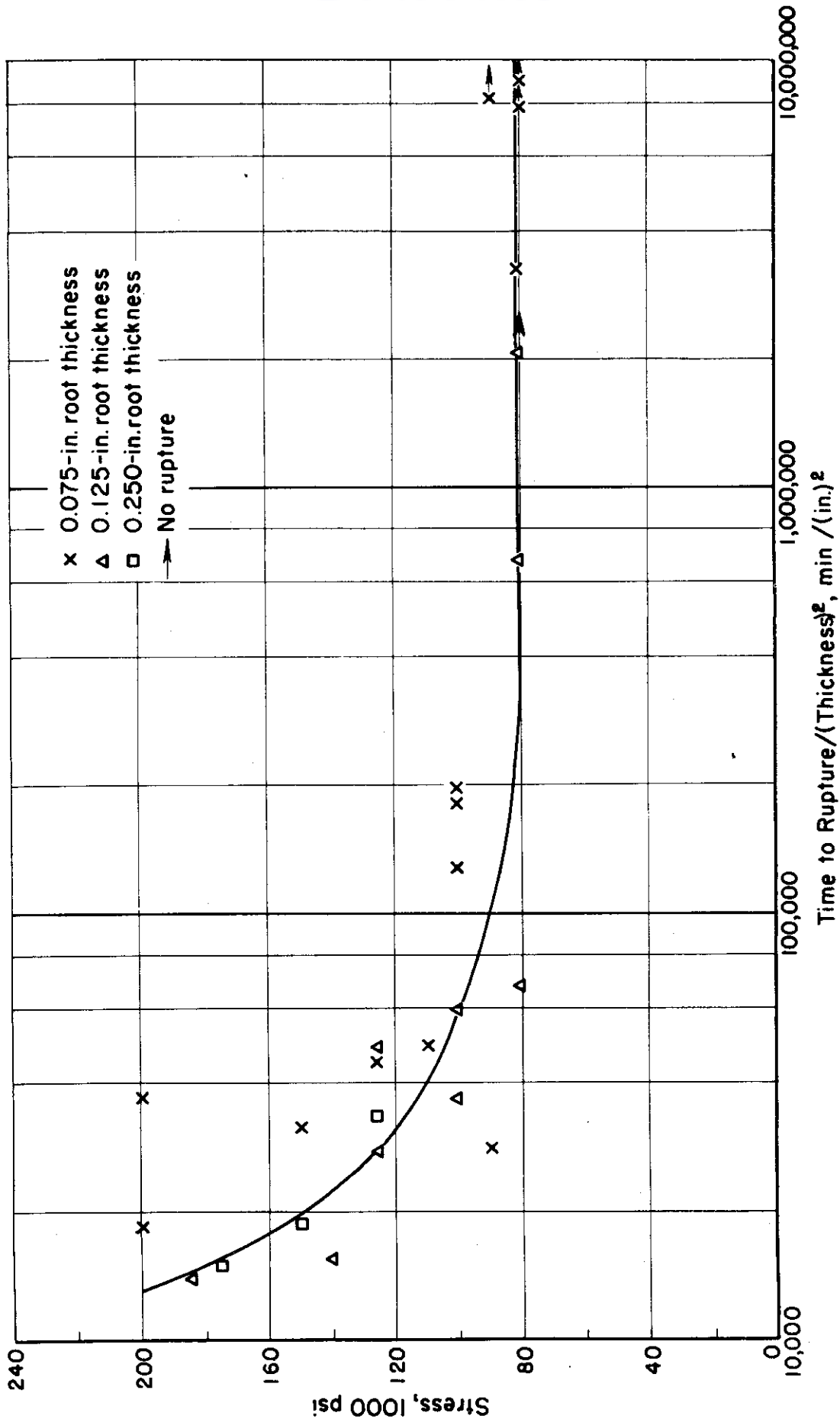


FIGURE 13. THE EFFECT OF SPECIMEN THICKNESS ON THE TIME TO RUPTURE OF NOTCHED SPECIMENS OF SAE 4340 STEEL LOADED IN BENDING WHILE BEING CHARGED CATHODICALLY WITH HYDROGEN IN A SULFURIC ACID ELECTROLYTE

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diameter of 5/8 inch. The central 2-1/2 inches had a wall thickness of either 0.037 inch or 0.0185 inch. The ends of these specimens had considerably thicker walls and were threaded to engage adapters. A tensile load applied to these adapters produced uniaxial tensile stress in the specimen.

A suitable cell was provided so that the thin-walled section of this specimen could be charged with hydrogen cathodically. The temperature of the cell during the electrolysis was maintained at 80 F.

The amount of hydrogen which diffused through the thin-walled section of the specimen was measured by the displacement of an inert liquid, n-butyl phthalate. Although n-butyl phthalate is reported to have a negligible solubility for hydrogen, molecular hydrogen was bubbled through it prior to each experiment. Also, the cavity within the specimen was filled with molecular hydrogen before each experiment.

After the beginning of the electrolysis, there was a period in which there was no measurable flow of hydrogen through the specimen. After this initial period, hydrogen was collected at an increasing rate until the steady-state condition appeared to have been achieved within an hour or two. A similar delay in the accumulation of hydrogen followed each change in the current density.

The data from these experiments first will be examined for consistency with the following assumptions: It is assumed that the amount of hydrogen collected is controlled by diffusion within the walls of this specimen, rather than by a surface reaction. It is further assumed that hydrogen escapes from the inner surface of the specimen so rapidly that the concentration there is very low.

The data for a typical experiment are plotted in Figure 14. If the straight-line portion of the curve is extrapolated to the time axis, the intercept "L" is obtained. According to Barrer⁽¹⁰⁾, "L" is a function of both the diffusion coefficient and the specimen geometry. Assuming the process to be controlled by diffusion, "L" should vary as the square of the specimen thickness. In Figure 14, "L" had a value of 64 minutes with a specimen wall thickness of 0.037 inch. For a specimen with a 0.0185-inch wall thickness, "L" had a value of 18 minutes. The theoretical value for the ratio of the two values of "L" is 0.25, while the observed value was 0.281. The difference between the two values of "L" was probably within the range of experimental error.

The flow of hydrogen through the permeability specimens was found to increase with time, as can be seen in Figure 14. Apparently, a steady-state condition of hydrogen flow was obtained in approximately 2 hours. However, in other experiments, after cathodic charging had been continued for 24 hours at a given current density, the flow rate of hydrogen through the specimen had increased to roughly twice the original "steady-state rate".

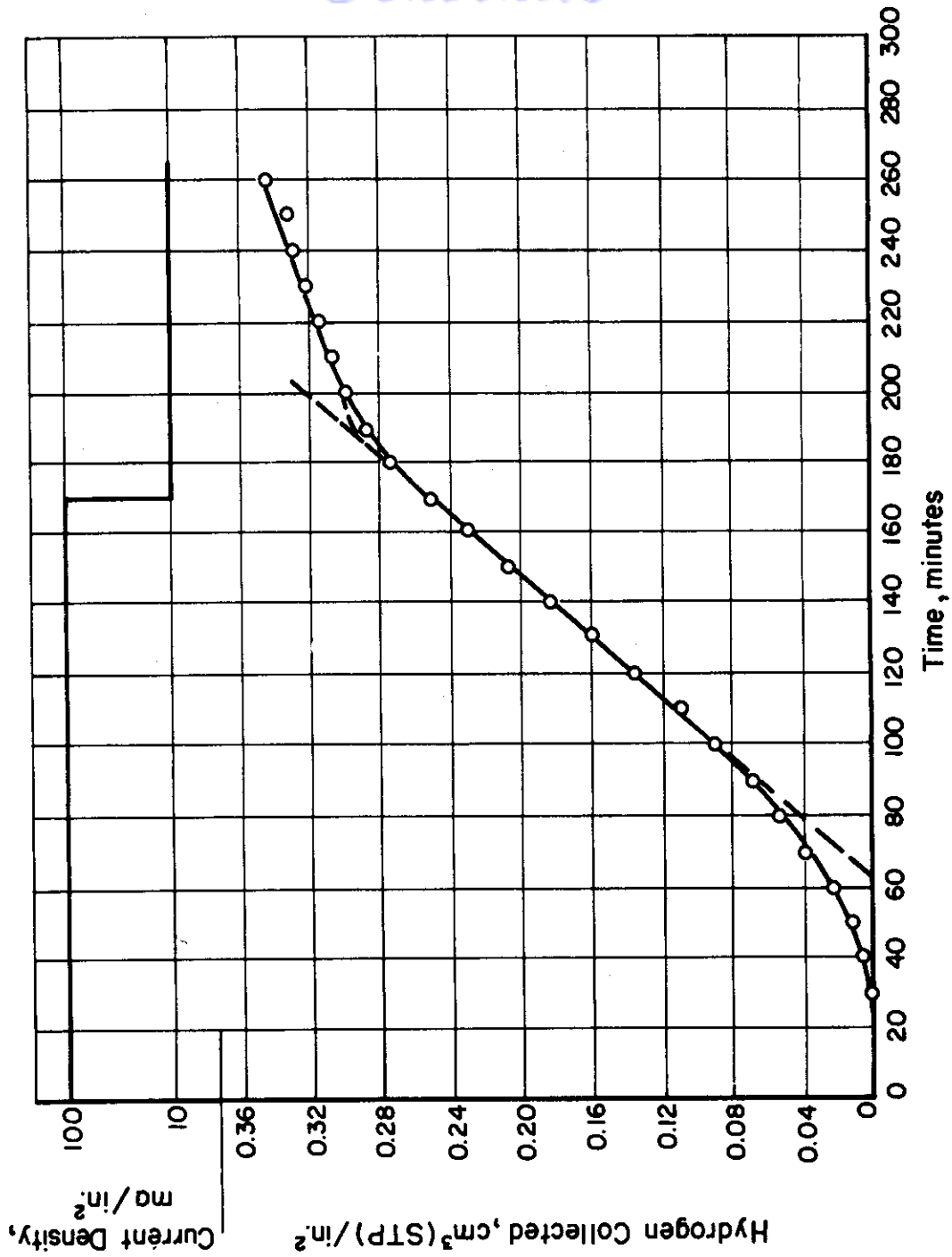


FIGURE 14. PERMEATION OF HYDROGEN THROUGH A 0.037-INCH WALL OF SAE 4340 STEEL DURING CATHODIC CHARGING IN A SULFURIC ACID ELECTROLYTE

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Conclusions

A similar behavior was noted on specimens with either a 0.037-inch or a 0.0185-inch wall thickness. This increase in flow rate with time also was noted both for the specimen during its initial cathodic charging and for the specimen which had been cathodically charged several times previously. For example, this effect was noted for the specimen which had been cathodically charged for a total of 24 hours during four preliminary experiments. After each of the preliminary experiments, the specimen had been baked at 340 F for 18 hours to remove hydrogen. As will be discussed in a later section of this report, a similar but more pronounced effect was noted when an alkaline electrolyte was used.

The effect of the wall thickness on the flow rate of hydrogen through the specimens for long and for short times was consistent with the assumption that the process was controlled largely by diffusion rather than by surface reactions. Increasing the wall thickness of the specimen by a factor of 2 reduced the flow rate of hydrogen to 1/2 of its original value.

The time required to reach the initial steady-state flow rate of hydrogen was considerably longer than the time required to reach the new steady-state flow rate of hydrogen after an abrupt change in current density. Also, the time required to obtain steady-state flow on decreasing the current was different from the time required when the current was increased. However, for a given change in current, after charging for a long time, both the time for obtaining a new steady-state flow rate and the new flow rate obtained were reproducible to a satisfactory degree.

Some further assumption must be made concerning the boundary conditions immediately following an abrupt change in charging conditions in order that the diffusion coefficient may be calculated. Two simple cases of the boundary conditions were considered. In Condition A, it was assumed that the concentration of the hydrogen at the entrance surface changed immediately from one equilibrium value to the other as the current was changed abruptly. In Condition B, it was assumed that the rate at which hydrogen entered the steel changed abruptly from the steady-state rate which corresponded to the initial charging conditions to the steady-state rate that corresponded to the final charging conditions.

It was noted that a longer time was required to establish steady-state flow when electrolysis was begun than after an abrupt change in current during electrolysis. Assuming either Condition "A" or "B" alone would suggest that the diffusion coefficient at the beginning of electrolysis was different than after some later change in current density. However, a single value for the diffusion coefficient can be obtained by assuming that something like Condition B exists at the beginning of the electrolysis and that something like Condition A exists after a change of current during electrolysis.

The effect of wall thickness upon the flow rate of hydrogen through the steel and upon the value of "L" supports the assumption that the controlling process in these experiments is diffusion within the steel rather than

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surface reactions. The difference in response of the flow rate following the initiation of electrolysis and after a subsequent change in electrolysis does not invalidate the assumption of a diffusion-controlled process.

When Condition B was assumed for the beginning of electrolysis, the calculated value for the diffusion coefficient was 10^{-6} cm²/sec and the hydrogen content at the entrance surface was calculated to be approximately 6 parts per million. This value for the hydrogen content is within the range of values reported for cathodically charged steel by the present observers and other investigators. This concentration of hydrogen was a result of cathodic charging of SAE 4340 steel heat treated to a tensile strength of 190,000 psi in a 4 per cent sulfuric acid electrolyte with a phosphorus poison and at a current density of 100 milliamperes per square inch.

An experiment was performed which indicated that a uniaxial tensile stress of 50,000 psi had no measurable effect on either the diffusion coefficient or the solubility of hydrogen in steel. This behavior was shown as follows: An unstressed specimen with a 0.037-inch wall thickness was cathodically charged at a current density of 10 milliamperes per square inch for 24 hours. The current then was changed abruptly to produce a current density of 30 milliamperes per square inch with the specimen remaining unstressed. After a steady-state flow of hydrogen had been obtained, the current was lowered to again produce a current density of 10 milliamperes per square inch and a tensile stress of 50,000 psi was applied. After an extended period, the current again was raised abruptly to produce a current density of 30 milliamperes per square inch. The steady-state flow rates of hydrogen at the high and low current densities and the times to obtain a steady-state flow rate of hydrogen following the abrupt change of current were unaffected by the stress, within the limits of experimental accuracy. These data are presented in Figure 15. The data have been plotted so that the origin of the time scale represents the time that the abrupt change of current density was made for both the stressed and unstressed conditions. The scale for the quantity of hydrogen collected was shifted so that the two curves coincided at zero time. Earlier experiments in which tensile stresses of 10,000 to 25,000 psi were applied before the beginning of the electrolysis also indicated that stress had no effect on the permeability of hydrogen in steel.

The influence of current density on the steady-state flow rate of hydrogen through a 0.0185-inch-thick specimen which was cathodically charged in the sulfuric acid electrolyte for 24 hours is shown in Figure 16. The influence of current density on the steady-state flow rate of hydrogen through a similar specimen which was cathodically charged in an acetic acid electrolyte is shown in Figure 17. The acetic acid electrolyte used was that described in an earlier section of this report on stress-rupture tests. It has been reported in the literature that permeability varies directly as the square root of the current density. While this relationship is not satisfied closely by the results obtained with the sulfuric acid electrolyte, the data for the experiment using the acetic acid electrolyte follow

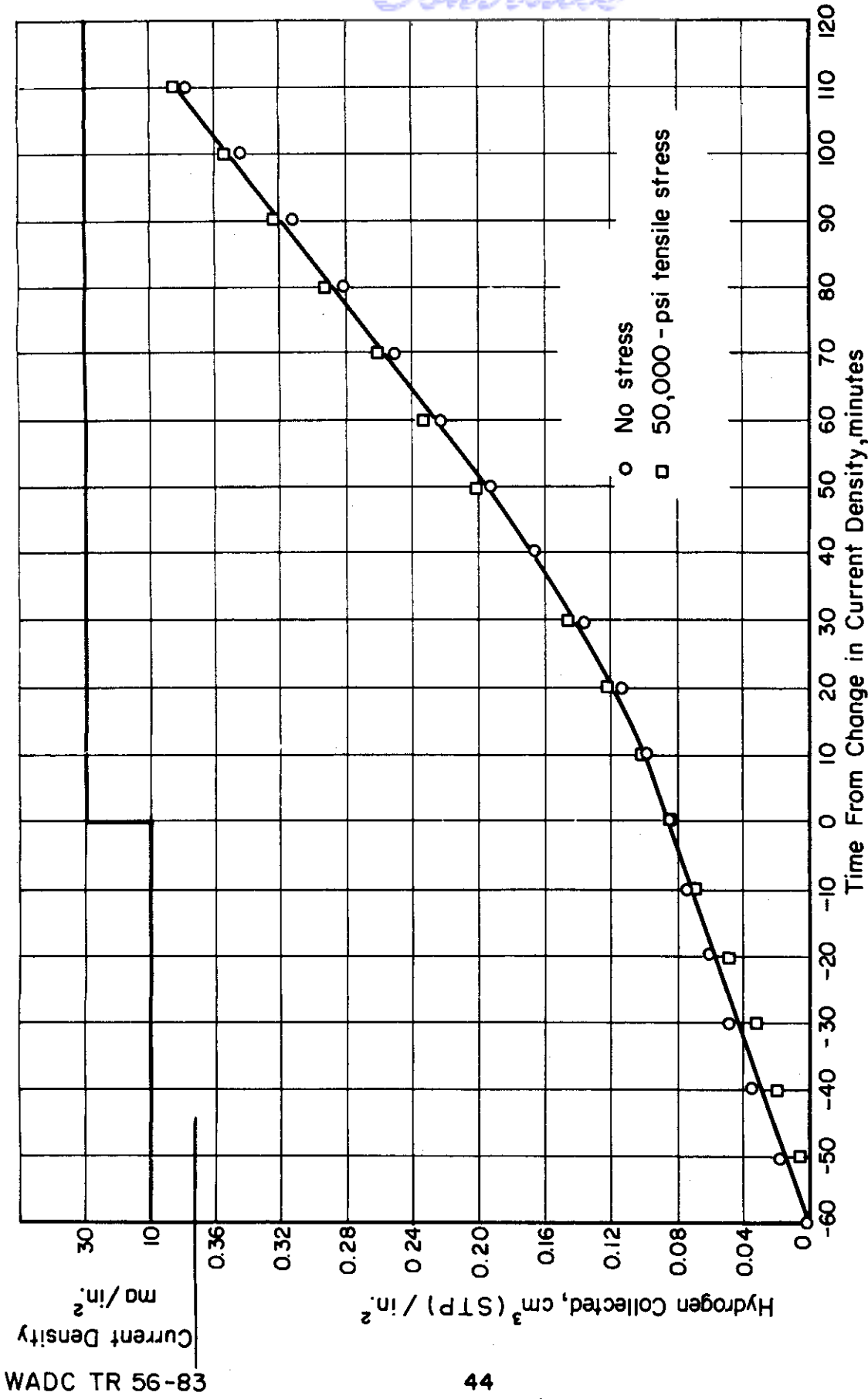
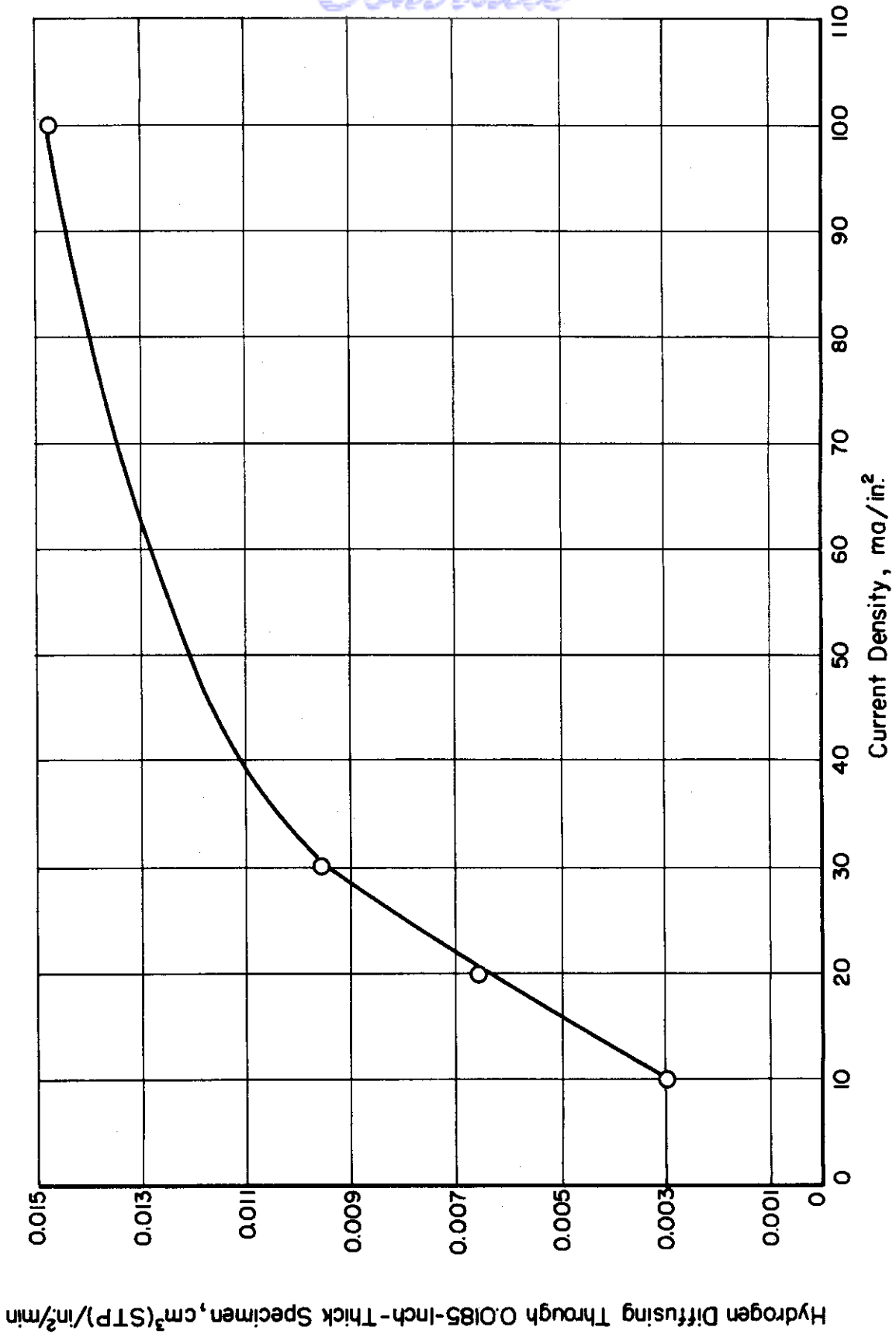


FIGURE 15. EFFECT OF TENSILE STRESS ON THE PERMEATION OF HYDROGEN THROUGH SAE 4340 STEEL DURING CATHODIC CHARGING IN A SULFURIC ACID ELECTROLYTE

A-13450



Hydrogen Diffusing Through 0.0185-Inch-Thick Specimen, cm²(STP)/in²/min

FIGURE 16. EFFECT OF CURRENT DENSITY ON THE PERMEATION OF HYDROGEN THROUGH SAE 4340 STEEL DURING CATHODIC CHARGING IN A SULFURIC ACID ELECTROLYTE A-13451

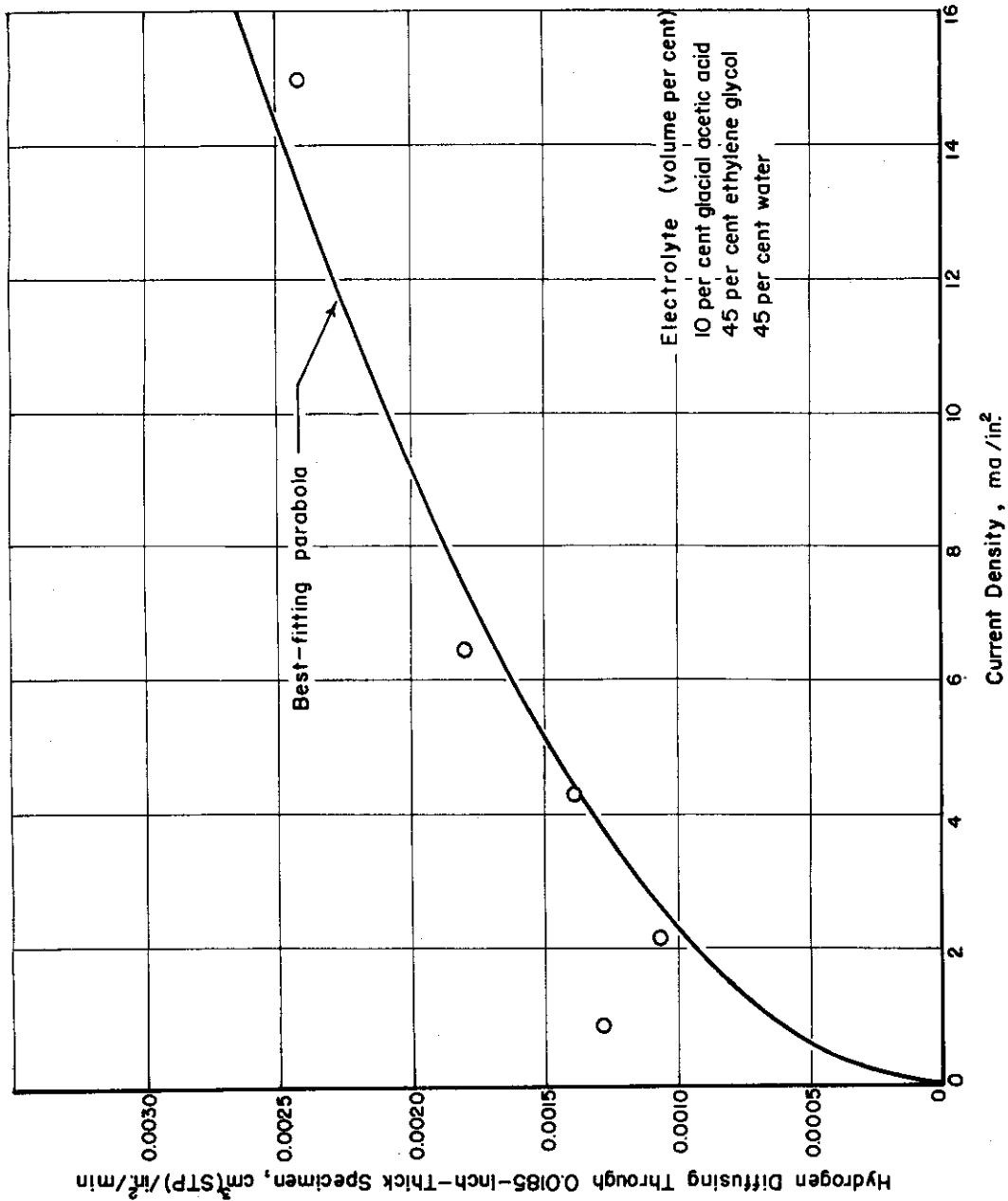


FIGURE 17. EFFECT OF CURRENT DENSITY IN AN ACETIC ACID ELECTROLYTE ON THE PERMEABILITY OF HYDROGEN THROUGH SAE 4340 STEEL A-17629

Conclusions

this relationship quite well for the range of current densities from 2 milliamperes per square inch to 15 milliamperes per square inch. For a given current density, the permeability was greater for the sulfuric acid electrolyte than for the acetic acid electrolyte. This strongly suggests that surface conditions as determined by the composition of the electrolyte affect the hydrogen content at the cathodically charged surface.

It was predicted from the stress-rupture behavior of this steel during cathodic charging that these permeability specimens would rupture in approximately 100 minutes or less at a stress of 50,000 psi. However, the permeability specimens did not rupture at the predicted time. Because only a limited number of specimens were available, only one specimen was cathodically charged intentionally until failure occurred. This specimen, which had a wall thickness of 0.0185 inch, was stressed to 50,000 psi tensile stress. Actual failure of the specimen was not observed, but time to rupture was more than 6 hours and less than 21 hours. Another specimen, with a wall thickness of 0.037 inch, was subjected to a stress of 30,000 psi for 6 hours during cathodic charging, and was examined metallographically. Cracks, 0.002 or 0.003 inch in depth, were found at the cathodically charged surface. The failure of these cracks to propagate through this specimen was attributed to the decreasing content of hydrogen with depth.

An experiment was conducted to study the effect of cadmium plating on the loss of hydrogen from steel. A permeability specimen with a wall thickness of 0.037 inch was cadmium plated with a cyanide bath on the inside only. It was intended that the cadmium plate would be 0.0005 inch thick. The steady-state flow of hydrogen through the specimen with the cadmium plate was approximately one-half that of a similar, but unplated, specimen charged under similar conditions. It should be noted that a similar decrease in the flow of hydrogen could have been achieved by increasing the thickness of the steel by approximately 0.037 inch. However, caution should be exercised in forming conclusions from this single experiment. It is reasonable to assume that various applications of cadmium plate could vary widely in their effectiveness in preventing the loss of hydrogen from steel.

An experiment was conducted to study the effect of cadmium plate on the absorption of hydrogen by steel during cathodic charging. A specimen was cadmium plated on the exterior surface only and baked at 340 F to remove the hydrogen introduced by plating. Cathodic charging of this specimen for 24 hours in the sulfuric acid electrolyte did not result in the accumulation of a measurable amount of hydrogen within this specimen.

Since it was desirable to perform stress-rupture tests with lower hydrogen contents than could be obtained by cathodic charging in an acid electrolyte, permeability tests were used in a search for charging conditions which would produce lower contents of hydrogen. Several electrolytes which consisted of buffered solutions of various organic acids or phosphoric acid were tested. These solutions were buffered to be either slightly acidic or slightly alkaline. Either sodium, potassium, or ammonium ions, or a

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combination of these were used to buffer the solutions. With these electrolytes and with the pH of the electrolyte between approximately 6 and 8, no measurable amount of hydrogen was collected in 24 hours. The electrolytes based on ammonium salts or on organic acids suffered the additional disadvantage of being decomposed, apparently, at the anode.

The lowest permeability was obtained with an electrolyte of a 1/2 per cent aqueous solution of sodium hydroxide. At a current density of 140 milliamperes per square inch, the flow of hydrogen through the specimen after 5 days' cathodic charging was about 1/5 that of the flow through the same specimen when an acetic acid electrolyte at a current density of 1 milliamperes per square inch was used. (This charging condition with the acetic acid electrolyte produced the minimum flow of hydrogen through the specimen for acid electrolytes.) With the sodium hydroxide electrolyte and a current density of 400 milliamperes per square inch, the flow of hydrogen through this specimen was about twice that obtained with a current density of 140 milliamperes per square inch.

However, data for the experiment using the sodium hydroxide electrolyte are not consistent with the results obtained using the sulfuric acid electrolyte. There was a major inconsistency which has not been explained at present. With the sulfuric acid electrolyte and a 0.0185-inch-wall specimen, a "steady-state" flow of hydrogen was obtained at approximately 1/2 hour, while with the sodium hydroxide electrolyte, no measurable amount of hydrogen was collected in that length of time. This might indicate that a surface condition and not diffusion within the specimen controlled the process. However, it is considered likely that the diffusion coefficient of hydrogen in steel is influenced by the structure and the recent history of the specimen with regard to hydrogen.

In the permeability experiments in which the sulfuric acid electrolyte was used, the flow rate of hydrogen increased for approximately 24 hours at a given current density, but with the sodium hydroxide electrolyte, the flow rate of hydrogen through the specimen increased for at least 5 days.

After 6 days of cathodic charging with the sodium hydroxide electrolyte, an abrupt change in the current densities was reflected in the collection of hydrogen within the specimen within 10 minutes. This is in sharp contrast to the length of time required to establish the initial flow of hydrogen using this electrolyte.

In acids, the permeability followed Fick's law of diffusion except that there was some increase of permeability with time. However, with the alkaline electrolyte, the deviations from the law were much more pronounced. The reasons for this behavior will be the subject of further study in this investigation.

HYDROGEN CONTENT AS A FUNCTION OF
CATHODIC CHARGING CONDITIONS

The information gained from the stress-rupture tests could be more generally applied if the rather arbitrarily chosen charging conditions could be correlated with an equilibrium hydrogen content. Therefore, a series of experiments was conducted in which samples of steel resembling the reduced section of the stress-rupture tests in both geometry and structure were charged cathodically under the conditions used in the stress-rupture tests. Since no measurable effect of stress on the solubility of hydrogen in steel was found in the permeability experiments, it was assumed that these specimens prepared for hydrogen analysis would have a hydrogen content and distribution similar to that of the stress-rupture specimen charged under similar conditions.

Specimens used in the hydrogen-analysis experiments were cylinders of the SAE 4340 steel described in the section on stress-rupture tests. This material had been processed to reduce the hydrogen content in a manner similar to that used for the stress-rupture specimens. The specimens were 0.250 inch in diameter by approximately 2 inches long to duplicate the reduced section of the stress-rupture specimens.

It was intended that the heat treatment of these specimens should duplicate the procedures used on the stress-rupture specimens. However, due to a mishap, air was admitted to the furnace during the first 10 minutes of austenitization, while for the following 30 minutes, the furnace chamber was evacuated to a pressure of about 10 microns. The specimens were quenched and tempered in the usual manner to produce an ultimate tensile strength of 230,000 psi. Unfortunately, time did not permit new specimens to be prepared and heat treated.

Following the heat treatment, the specimens were aged at room temperature from 4 to 17 days prior to cathodic charging. The electrolytes, time, and current density used during cathodic charging are shown in Table 4. The anode during this series of experiments consisted of sixteen 30-gage-platinum wires arrayed as elements of a cylinder concentric with the specimen. Following the cathodic charging and aging, if used, the specimens were stored in liquid nitrogen until analysis.

The hydrogen analyses of these specimens were conducted by a vacuum-fusion method which is described in the literature^(11,12).

The conditions of charging and aging and the results of these experiments are presented in Table 4.

A statistical study of the results by an analysis of variance for testing significance showed a significant difference at the 5 per cent level of

TABLE 4. HYDROGEN CONTENT OF AN SAE 4340 STEEL (230,000 PSI ULTIMATE TENSILE STRENGTH)
AFTER VARIOUS CATHODIC CHARGING CONDITIONS

Cathodic Charging Conditions			Aging Time at Room Temperature, days(a)	Hydrogen Content, ppm(b)	
Electrolyte	Current Density, milliamperes/in. ²	Time, hours			
-	(Not charged)	-	18	0.4	1.3
4% sulfuric acid and poison	100	24	0(c)	3.7	6.5
4% sulfuric acid and poison	8	24	0	6.7	8.6
4% sulfuric acid and poison	8	48	0	1.8	
4% sulfuric acid and poison	8	24	10	0.5	
4% sulfuric acid and poison	8	24	3	0.3	
4% sulfuric acid and poison	8	24	2	0.6	
1/2% sodium hydroxide	500	24	0	0.6	
1/2% sodium hydroxide	500	336	0	2.9	5.0
1/2% sodium hydroxide	125	336	0	0.8	2.1

(a) For uncharged specimens, time reported was time from final heat treatment until storage in liquid nitrogen prior to analysis. Aging time for all other samples was time from completion of charging until storage in liquid nitrogen.

(b) Two values indicate results of duplicate tests - cathodically charged and analyzed separately.

(c) Indicates that specimen was stored in liquid nitrogen within 3 minutes of completion of cathodic charging.

probability. However, the reliability of this was uncertain due to the small number of tests. Therefore, any interpretation of the results must be accepted with caution.

The hydrogen contents which resulted from three charging conditions (charging in the sodium hydroxide electrolyte at current densities of 125 milliamperes per square inch and 500 milliamperes per square inch, and charging in sulfuric acid at a current density of 8 milliamperes per square inch) increased in the order in which the conditions are listed. When stress-rupture tests involving those charging conditions are considered, the minimum stress for failure decreased in the same order. That is, the loss of strength during cathodic charging appeared to increase with increasing hydrogen content.

The existence of "residual" or "nondiffusible" hydrogen was indicated. After charging for 24 hours at a current density of 8 milliamperes per square inch in sulfuric acid, two specimens had average hydrogen contents of 7.6 ppm. Aging at room temperature for from 2 to 10 days reduced the hydrogen content of similar specimens to approximately 0.5 ppm.

It also was noted that hydrogen which was in the steel after heat treatment was not eliminated completely at room temperature in 18 days. Although little confidence can be placed in this observation, it was noted that the average hydrogen content of the three specimens which were cathodically charged and aged from 2 to 10 days was less than the average hydrogen content of the heat-treated but not charged specimens which had been aged for 18 days. The residual hydrogen contents of the heat-treated samples were higher than those reported by Derge, Peifer, and Richards⁽⁶⁾ for steel rails.

In the permeability experiments, the flow of hydrogen through the specimen charged at 8 milliamperes per square inch in sulfuric acid was approximately 6 times as large as the flow through the specimen charged at 500 milliamperes per square inch in the sodium hydroxide electrolyte, and it was expected that the hydrogen contents would have the same ratio. However, the hydrogen content for those charging conditions of electrolyte and current density and for times of 24 and 336 hours, respectively, are in the ratio of roughly 2. The longer time, 336 hours for the sodium hydroxide electrolyte, was used as a basis for comparison, because the permeability experiments indicated that steady-state permeability was achieved with the alkaline electrolyte only after a much longer time than with the acid electrolyte.

The maximum hydrogen content reported was for the specimens charged at 8 milliamperes per square inch in sulfuric acid for 24 hours. It was anticipated that 24 hours cathodic charging would result in a hydrogen content which approached the supposed equilibrium hydrogen content for these charging conditions. It was anticipated that longer charging times

under these conditions would result in little change in hydrogen content. However, the specimen charged for 48 hours had a much lower hydrogen content.

From the results of the permeability experiments, it was anticipated that the specimen charged in the sodium hydroxide would require considerably longer to approach an equilibrium hydrogen content than would a specimen charged in sulfuric acid electrolyte. Although the specimen charged in sulfuric acid did not approach an equilibrium content, it apparently had a maximum hydrogen content at some time less than 48 hours. As anticipated, the specimen charged in sodium hydroxide for 336 hours contained more hydrogen than the specimen charged for 24 hours.

These data, which contain several apparent contradictions, could best be rationalized by assuming the existence of "nondiffusible" hydrogen which varies in a complex manner with the history of the specimen and which does not affect the diffusion of hydrogen in the steel, and also the existence of a diffusion coefficient which varies with the specimen history. Sims⁽⁷⁾ reviews evidence of the existence of different modes of diffusion of hydrogen in steel. Johnson and Hill⁽¹³⁾ observed that the existence or absence of "residual" hydrogen depended upon the thermal history of the specimen.

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