NACA TN 2696 3063

TECH LIBRARY KAFB, NM
0065755

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2696

A FUNDAMENTAL STUDY OF THE MECHANISM BY WHICH HYDROGEN ENTERS METALS DURING CHEMICAL AND ELECTROCHEMICAL PROCESSING

By L. D. McGraw, C. A. Snavely, H. L. Moore
P. T. Woodberry, and C. L. Faust

Battelle Memorial Institute

Washington
April 1952

AFMDC
TECHNICAL LIBRARY
AFL 2811

TECH LIBRARY KAFB, NM
0065755

TABLE OF CONTENTS

Page

SUMMARY 1

INTRODUCTION 1

EXPERIMENTAL WORK 2
Identification of So-Called "Nascent" Hydrogen as a Metal-Hydrogen Alloy 2
Hydrogen Entry in Basis Metal Associated with High-Efficiency Plating Baths 4
Relation of Inclusions in Copper to Susceptibility to Embrittlement 5
Effect of Arsenic (if Present) in Reduction of Heavy Metals during Electrodeposition 6
Effect of Promoter Elements on Bubble Formation during Cathodic Pickling 8
Inhibition of Hydrogen Embrittlement during Cathodic Pickling and Its Relation to Catalytic Decomposition of Hydrogen Alloys 10
Oxidizing Agents as Inhibitors of Embrittlement Incurred during Pickling and Metal Deposition 12
Catalytic Effects Related to Efficiency of Oxidizing Agents as Inhibitors of Embrittlement 14
Phase-Boundary Reactions Involving Free Radicals 16
Envelope Protection of Metals Susceptible to Embrittlement by Metals Impermeable to Hydrogen 22

DISCUSSION 22
Results 22
Newly Proposed Mechanism 24

APPENDIX A - LITERATURE SURVEY 25
Other Proposals Related to Entry Mechanism 25
Evidence for Newly Proposed Mechanism Based on Earlier Literature 26

APPENDIX B - MEASUREMENT OF HYDROGEN EMBRITTLEMENT 31
Apparatus 31
Choice and Preparation of Suitable Specimens 31
Determination of Reliability of Constant-Rate Bend Test as an Indication of Relative Hydrogen Content 31

REFERENCES 33

TABLES 35

FIGURES 41

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2696

A FUNDAMENTAL STUDY OF THE MECHANISM BY WHICH HYDROGEN ENTERS METALS DURING CHEMICAL AND ELECTROCHEMICAL PROCESSING

By L. D. McGraw, C. A. Snavely, H. L. Moore
P. T. Woodberry, and C. L. Faust

SUMMARY

Several known methods of controlling the entry and exit of hydrogen in steel were correlated with the known chemical behavior of atomic and molecular hydrogen. Through this correlation, suitable reagents were found which increase or, for the first time, significantly decrease hydrogen permeability and embrittlement of SAE 4130 and other steels during cathodic pickling and of spring steel during zinc and cadmium plating without lessening the apparent quality of the pickling or the plating. This successful correlation was an important step toward arriving at the mechanism of hydrogen entry into steel. The same data showed that the diffusion of hydrogen in steel and the freedom of exit of hydrogen are also important in determining the extent of embrittlement. Heretofore, the separate importance of entry and exit has not been clearly recognized and subjected to independent control. The phenomena are chemical and not mechanical. Entry is through the direct formation of metal hydrides (intermetallic compounds) or solid solutions of hydrogen in metal at the instant of hydrogen discharge. Exit is the decomposition of metal hydrides or of solid solutions of hydrogen in metal. The rate of accumulation of hydrogen in the metal is dependent on the relative speeds of entry, diffusion, and exit under whatever environmental conditions prevail.

INTRODUCTION

The detrimental effects of hydrogen in metals are well-known and are reflected in such physical properties as ductility, tensile strength, and fatigue strength and in behavior and performance of surface coatings, both metallic and nonmetallic. The disposition of hydrogen in metals, particularly steel, has been the subject of many recent papers. Various hypotheses have been advanced relating to the location of the hydrogen

inside the steel and to how hydrogen exerts its damaging effects. Other papers have reported thermodynamic data relating to the formation of molecular hydrogen and its availability at metal surfaces. Still other researches have reported physical conditions of treatment to introduce hydrogen into metals as demonstrated by subsequently measured changes in the properties of the metals.

No previous work, however, has come to the attention of the present authors where an adequate explanation has been given of the mechanism of the process by which hydrogen leaves the molecular or ionic phase and enters the metal, presumably as free atoms. (See appendix A for a discussion of some other proposals.) Further knowledge of this mechanism, it is believed, should be of value in any effort directed toward improving pickling and plating practices so as to reduce below the harmful level, or eliminate, any hydrogen pickup by the basis metal; for this reason the present fundamental study was undertaken.

This investigation was conducted at the Battelle Memorial Institute under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

EXPERIMENTAL WORK

The experiments which were conducted to determine the mechanism of hydrogen entry, and from which were found reagents that increase or decrease the hydrogen permeability of steels during pickling or plating, are described in this section. The order of presentation of the experiments is designed to show in logical sequence the various steps necessary to support the proposed mechanism. Pertinent comments and conclusions are given in the "Remarks" sections immediately following the experiments to which they apply.

Identification of So-Called "Nascent" Hydrogen as a Metal-Hydrogen Alloy

Experiment 1, preparation of copper hydride (CuH).- If hydrogen must react with metals to enter them, the exit of hydrogen from metals should correspond in all respects to the decomposition or chemical destruction of metal hydrides (the intermetallic compounds) and solid solutions of hydrogen in metal. The object of preparing copper hydride was to use it to compare the decomposition of hydrides with the loss of hydrogen from cathodically charged metals. The comparison may be shown by catalytic or by chemical reaction.

The copper hydride was prepared as follows (see references 1 and 2): An almost saturated aqueous solution of 33 grams of sodium hypophosphite was added to a solution of 25 grams of copper sulfate pentahydrate and 10 milliliters of sulfuric acid (sp. gr., 1.84) in 90 milliliters of water. The solution was heated to 122° F and held at this temperature for 15 minutes. The copper-hydride solid reaction product was purified by repeatedly stirring it in fresh, distilled water and decanting the supernatant liquid. It was concentrated either by filtration or decantation but was never dried.

Experiments 2 and 3.- These tests were designed to compare the chemical activity of a metal hydride with that of the so-called "nascent" hydrogen produced during chemical or electrochemical reactions involving a metal surface. The experimental conditions follow.

A slurry of CuH in water was shaken intermittently with chemically pure carbon tetrachloride (CCl_4) for 15 minutes. Then, the supernatant liquid was filtered free of CuH. The filtrate gave a positive test for chloride ion with silver nitrate,

$$2CuH + CCl_4 \rightleftarrows 2Cu + HCl + CHCl_3$$

A 1-milliliter portion of the filtrate was treated with a few drops of aniline and a pellet of sodium hydroxide (NaOH). A strong positive test for chloroform $(CHCl_3)$ was obtained, that is, the unmistakable odor of phenylisocyanide, according to

$$C_6N_5NH_2 + CHCl_3 + 3NaOH \longrightarrow 3NaCl + 3H_2O + C_6H_5\text{-}N = C$$

As a control, the same reagents were added to a mixture of CCl_4 and water which had not been shaken with CuH. The tests for chloride and $CHCl_3$ were negative.

Experiment 4.- A chemical reaction between carbon tetrachloride and atomic hydrogen in palladium was shown by the following test: Palladium, charged with hydrogen, was added to a solution of silver nitrate saturated with carbon tetrachloride. A film of black, silver metal was first seen to form on the surface of the palladium (direct reduction of silver). This was followed by the rapid formation of a heavy film of silver chloride on the metal. The latter product was the result of displacing the equilibrium,

$$H\cdot + CCl_4 \rightleftarrows HCl + \cdot CCl_3$$

to the right by reaction of the product (HCl) to form silver chloride.

Remarks.- The results of the four experiments show that hydrogen "in" metals, as proposed in this report, can reduce carbon tetrachloride. It may be concluded from this fact that the concept of nascent hydrogen is not necessary to account for the reduction of organic compounds by the action of acids on "active" metals, such as zinc, cadmium, and so forth. Copper would not liberate such hydrogen from acids, because it is below hydrogen in the electromotive series and cannot be considered an active metal.

Hydrogen Entry in Basis Metal Associated with High-Efficiency Plating Baths

Many copper plating baths are said to have a high cathode efficiency because codeposition of hydrogen is not observed during their operation. This is a very poor criterion to use, as may be seen from the following experiments. Also, hydrogen embrittlement has been reported from 100-percent copper-deposition current efficiency.

Experiments 5, 6, and 7.- When copper was plated on a platinum cathode at 60 amperes per square foot and 90° F from a chloride bath, little or no hydrogen was evolved. The copper plate was contaminated with considerable cuprous chloride (CuCl), as was shown by X-ray spectrographic analysis and by the fact that the deposit melted easily in the flame of a laboratory gas burner. The plating bath composition and operating conditions were as follows:

Cupric chloride ($CuCl_2 \cdot 2H_2O$), mole/liter	1
Boric acid, grams/liter	30
pH	4
Anode	Copper
Cathode current density, amperes/sq ft	10

Experiments 8 and 9.- When the contaminated copper deposit was made cathodic in 10 percent sulfuric acid, no hydrogen was evolved on it for an initial period of time depending on current density of hydrogen deposition and the thickness of the contaminated copper. At the time hydrogen evolution began, the pastel pink deposit had changed to a characteristic copper red.

The cathodic reduction of inclusions in electrolytic copper robbed current from cathodic areas which did not contain such inclusions. One-half the length of a Cu-CuCl codeposit was made cathodic in 10 percent sulfuric acid until hydrogen was evolved vigorously on it. Then, the entire cathode was immersed into the bath, and hydrogen evolution stopped completely until the upper half of the deposit was reduced. At that time, hydrogen evolution began over the entire cathode.

Experiment 10.- It is well-known that far less than 1/2 percent chloride in an acid and copper-sulfate bath is sufficient to promote cuprous-chloride (CuCl) inclusions. An acid and copper-sulfate bath containing 1/2 percent sodium chloride gave a copper deposit, under normal operating conditions, which did not evolve hydrogen for 6 seconds when made cathodic in a 10-percent sulfuric-acid solution at a current density of 25 amperes per square foot.

Relation of Inclusions in Copper to Susceptibility to Embrittlement

It is not known whether the electrolytic reduction of inclusions in metal plating can promote embrittlement of the basis metal. It is known (reference 3) that oxygen in solid solution and precipitated as cuprous oxide (Cu_2O) in copper makes copper susceptible to hydrogen embrittlement. Similarly, metals (arsenic, antimony, and bismuth) and foreign oxides also make copper susceptible to hydrogen embrittlement. The severity increases with the ease of reduction of the oxide. Copper is not embrittled if oxygen, arsenic, bismuth, and so forth are removed.

Mantell (reference 4) reports on the analysis of the electrolyte (0.012 percent chloride) and copper cathode (0.157 percent chloride) for electrowon copper. Adsorbed gases total 0.01 percent with aluminum oxide (Al_2O_3) and ferric oxide (Fe_2O_3) totaling 0.113 percent. This explains the high efficiency of the electrowinning operation, because hydrogen is not evolved on copper containing chloride inclusions.

The following experiments were conducted to study the hydrogen content of copper containing electrolytically reduced inclusions.

Experiment 11.- Cuprous chloride was cast into sticks for use as cathodes in 10 percent sulfuric acid. When the surfaces of the sticks were partially reduced, they conducted well, and the salt could be completely reduced electrolytically without hydrogen evolution, yet the copper acquired hydrogen. The copper formed in this way was washed with dilute sulfuric acid. The washings contained no material oxidized by methylene blue, but the copper rapidly reduced methylene blue to its leuco base, showing that the copper held active hydrogen similar to that in copper hydride.

Experiment 12, electrolytic decomposition of hydrides.- This experiment was conducted to determine whether the catalytic decomposition of a hydride can be duplicated by normal conditions of electrolysis. The experimental conditions were as follows:

A platinum cathode was placed in a test tube containing a heavy slurry of copper hydride. The test tube, which had a hole in its side, was placed in a 10-percent sulfuric-acid solution. Deposition of hydrogen on the platinum cathode was carried out at 0.5 ampere at 86° F. Very little hydride was carried out of the test tube into the bath proper by the gas evolved. As a result of electrolysis, the slurry of powdery hydride was converted to a metallic copper sponge which clung to the platinum electrode when it was removed from the test tube. The copper sponge did not evolve hydrogen, as CuH would, when it was placed in a 10-percent sodium-hydroxide solution. It may be concluded that CuH, formed at a cathode in an acid solution, decomposed as fast as formed if hydrogen also was being codeposited. The reason was the basic or less acid nature of the solution around the cathode. In addition, it is apparent that the cathodic pickling of metals is less embrittling in an alkaline solution than in an acid solution because the hydrogen is released from the metal as rapidly as it enters. The new mechanism of this report proposes that hydrogen enters through formation of an alloy and leaves by decomposition of the alloy. The same intermetallic compound or solid solution so formed is catalytically destroyed by hydroxide ion (OH^-). Whenever a proton (H^+ ion) discharges at a metal surface in aqueous mediums, an excess of OH^- remains.

Remarks.- Current-efficiency calculations for copper plating from the acid-sulfate bath are based on divalent copper. Copper hydride can codeposit with the copper. Copper hydride will have the same weight, within the weighing limitations of usual plating experiments, and will use up the same number of coulombs as deposition of Cu^{2+}. Hence, the current efficiency would show the same as though all copper deposited from Cu^{2+}.

The CuH is unstable, so it can give up its hydrogen to enter steel, until a continuous copper coating is reached. Then, no additional hydrogen enters the steel. In any case, the amount of hydrogen is small, so only extremely "sensitive" steels can be affected.

By analogy to the above, hydride formation of the depositing metal during metal deposition can account for embrittlement, even when there is no apparent discharge of hydrogen. Electrodeposition of metal hydrides has been experimentally observed in other work. (See references 5 to 7.)

Effect of Arsenic (if Present) in Reduction of Heavy Metals during Electrodeposition

Experiments 13 to 19.- These experiments were conducted to study what part arsine (AsH_3) might play in the deposition of heavy metals

from solutions contaminated with arsenic. This was of special interest because of the relative ease of reduction of such metals compared with arsenious hydride (arsine) formation.

The plating baths used were as follows:

I - Copper:

Cuprous cyanide, grams/liter	26.9
Sodium cyanide, grams/liter	35.4
Sodium carbonate, grams/liter	30.8
Sodium hydroxide, grams/liter	6.8
Rochelle salt, grams/liter	30.8

II - Arsenic:

Arsenious oxide, grams/liter	123.0
Sodium hydroxide, grams/liter	123.0
Sodium cyanide, grams/liter	3.9

The recommended operating conditions for the two baths were:

	I - Copper	II - Arsenic
Anode	Copper	Steel
Cathode current density, amperes/sq ft	20 to 60	3 to 20
Tank voltage, volts	2 to 3	2.5 to 4
Temperature, °F	140 to 160	75 to 85

Arsenic was elctrodeposited on steel from bath II at the low end of the current-density and tank-voltage ranges because, at the high end of the range, the deposits were loose and were swept off the basis metal by hydrogen evolution (cathodes were 1- by 3-in. steel panels, anode was a 3- by 3-in. steel panel). The arsenic deposits (0.4 mil thick) were copper plated at 36 amperes per square foot (cathode and anode current density) for 3 minutes, and then at 18 amperes per square foot for 3 minutes. The resulting deposit was found by X-ray diffraction analysis to be composed of copper plus cuprous arsenide (Cu_3As) in the surface layers. Spectrographic analysis showed the presence of both copper and arsenic in the surface of the plate.

Electrolysis of a solution prepared by mixing equal volumes of plating baths I and II gave a deposit of pure Cu_3As (X-ray diffraction analysis accurate to ±5 to ±10 percent on the absence of free copper or arsenic) under the following plating conditions:

Cathode and anode	Steel (1/64 by 1 by 3 in.)
Cathode current density, amperes/sq ft	20 to 25
Tank voltage, volts	2 to 3
Temperature, °F	130 to 140
Time, hr	0.5

The approximate thickness of the deposit was 0.3 mil.

The results of the tests show clearly that copper was deposited substantially as Cu_3As on an arsenic cathode and was also deposited in the same form on a steel cathode where the plating bath was contaminated with arsenic in sufficient amounts.

Remarks.- The only conclusion which may be taken from these results is that the Cu_3As is formed by precipitation of copper from solution by cathodically formed arsine, unless copper diffuses as rapidly, which it does not, in arsenic as hydrogen does in metals in which it is soluble. Thus, hydrogen reacts like a metal with the metal arsenic to form the "gaseous" intermetallic compound arsine, AsH_3. Experiments 2 and 3 showed that hydrides can reduce other substances.

There was no evidence of excess copper, in spite of the high rate at which the metal was being reduced. Hence, all the copper was chemically reduced by arsine formed at the cathode, and none was deposited by simple electron transfer.

Effect of Promoter Elements on Bubble Formation during Cathodic Pickling

Experiments 20 to 24.- These experiments were conducted to observe what changes occur in the character of the hydrogen bubble formation on cathodic surfaces when embrittlement promoters are present in the pickling bath or when the cathode surface has been "poisoned" with embrittlement promoters. The experimental conditions were as follows:

Using a platinum anode, arsenic was plated on a 5/8-inch strip of copper for 20 minutes at 2.5 volts at 5 to 10 amperes per square foot and 76° F. The plated copper strip was then used as the cathode in a 10-percent sulfuric-acid bath at 82° F with a platinum anode. Almost the entire cathode surface was covered with small bubbles of hydrogen which were in contact with one another, thus leaving little solution in contact with the metal. A few bubbles grew more rapidly than the others; when they became quite large, they left the surface of the vertical electrode with an upward sliding motion instead of passing out

horizontally into the solution. In so sliding, they removed all the gas in their path, leaving streaks of exposed metal. Immediately, a uniform "fog" of fresh bubbles formed in these streaks. The fresh bubbles grew fairly uniform in depth until one or more repeated the sweeping cycle. Even at a high current density (110 amperes/sq ft), bubbles did not leave the cathode much faster than they could be counted.

An untreated copper strip, used as a cathode in the acid bath above, behaved quite differently. The gas was evolved as a fine spray when the cathodes were vertical or bent 90° so that a portion was horizontal. The bubbles were too small and too numerous to be seen forming, and few grew large enough and slowly enough to be seen leaving the cathode. The gas formed at small points and covered very little cathode area. The same metal, treated by coupling with zinc metal in 10 percent sulfuric acid containing 0.07 gram per liter of arsenious oxide (As_2O_3) and then rinsed, gave the same bubble formation previously described for the arsenic cathode when treated in the sulfuric-acid pickling bath.

The effect of phosphorous upon bubble formation was shown to be the same as the effect of arsenic by the following experiment. A copper strip was cleaned by dipping in 1:5 nitric acid and rinsed. Hydrogen was plated on it at 110 amperes per square foot from an orthophosphorous-acid solution (30-percent solution diluted to five times its original volume) for approximately 1 minute. After rinsing, hydrogen was plated on it from a 10-percent sulfuric-acid bath. The same type of bubble formation, characteristic of plating hydrogen on an arsenic-plated panel, was seen for current densities from 2 to 110 amperes per square foot.

There was also a change in the contact angle of the bubbles when arsenious oxide was in the pickling acid. At 85° F, the contact angle of hydrogen bubbles on a horizontal copper cathode in 10 percent sulfuric acid was 120° to 125°. With arsenious oxide present in the acid to the extent of 0.09 gram per liter, the contact angle was 100° to 105°. The contact angles were measured on the calibrated ground-glass plate of a camera onto which the magnified silhouettes of the bubbles were projected.

Greater potentials were required to maintain a given current density when arsenic was present owing to the overpotential built up by the accumulations of hydrogen in the cathode. Near 110 amperes per square foot, the cell voltages were 4.9 and 3.5 volts with arsenic and copper cathodes, respectively. At 2.5 amperes per square foot, the corresponding voltages were 2.7 volts and 1 volt.

These observations were extended to include carbon tetrachloride, another promoter of embrittlement. This compound changed the character of bubble formation just as arsenic did. The effect of carbon tetrachloride on overpotential was also noted. The potential of a low-carbon

steel cathode was measured against a saturated calomel electrode when the steel was cathodic (current density, 1 ma/cm^2) in a 2N sulfuric-acid solution (pH = 0.58) at 80° F. The measured potential of 0.408 volt was raised to 0.545 when carbon tetrachloride was added to the acid bath.

The results of these experiments show that the increase in hydrogen overpotential following the addition of embrittlement promoters to the cathodic pickling baths was associated with a change in the character of hydrogen-bubble formation on the surface of the metal being pickled (fig. 1).

Remarks.- It may be concluded from these tests that this change in character of the cathodically formed hydrogen bubbles is in some measure responsible for increased rate of entry of hydrogen into pickled metals. Even intuitively, an observer would expect the dense uniform fog of gas seen on the cathode (fig. 1) when arsenic is in the bath to introduce more gas into the cathode than the few small bubbles leaving scattered points on the cathode surface in the absence of arsenic. The results also imply that these poisons give the cathode surface a uniformly high overpotential for hydrogen by poisoning scattered areas of low overpotential.

Inhibition of Hydrogen Embrittlement during Cathodic Pickling and Its Relation to Catalytic Decomposition of Hydrogen Alloys

Experiments 25 to 42.- According to the new mechanism of hydrogen entry into metals, reagents which catalyze the decomposition of copper hydride should inhibit embrittlement incurred during cathodic pickling of metals. The experiments described here and in table 1 were performed to check the validity of this conclusion. The method used for measuring the extent of hydrogen embrittlement as a test of the processes under study for hydrogen entry and exit is described in appendix B.

The following baths were used for the cathodic pickling experiments:

Bath A - 10-percent sulfuric-acid solution - 10 volumes of sulfuric acid (sp. gr., 1.84) to 90 volumes of water

Bath B - Sodium-hydroxide solution - 10 percent by weight

Bath C - Solution of 10 grams of citric acid monohydrate, 10 grams of aluminum sulfate $\left(Al_2(SO_4)_3\right)$, and 90 grams of water

Bath D - Solution of 11.7 grams of Rochelle salts, 10 grams of $Al_2(SO_4)_3$, and 90 grams of water

Bath E - Solution of 10 grams of sodium carbonate and 12 grams of citric acid monohydrate per 100 milliliters of solution

The data of table 1 show that citrate and hydroxide inhibited embrittlement. They also show that the inhibition of embrittlement by anions was extended to highly acid solutions in the case of the complex salts of aluminum with citric and tartaric acids. This latter result is most important, because cathodic pickling is not effective in alkaline solution. The aluminum salts reduced hydrogen entry during pickling in acid solutions.

Solutions of complex salts of aluminum with citric and tartaric acids decomposed copper hydride just as fast as alkaline solutions when the pH was as low as 4.5, and were still effective at a pH of 2 (experiment 42). This is good evidence that their action was an extension of the normal catalytic activity of citrate and tartrate at high pH.

Remarks.- It may be concluded from the results of these experiments that the catalytic decomposition of copper hydride in the presence of any chemically inert ion is an indication that the same ion will inhibit entry of hydrogen into other metals. Furthermore, some anions which catalyze copper-hydride decomposition only in a basic solution can be modified, by complex formation, so as to be effective in an acid solution. These same complex ions will inhibit entry of hydrogen into a metal (and reduce embrittlement).

If tartrate, citrate, and so forth are effective inhibitors, reducing hydrogen entry, they should diminish hydrogen entry (and embrittlement) when added to plating baths. This postulate was tested in the following experiments.

Experiments 43 and 44.- Tartrate, without being complexed with aluminum, should inhibit embrittlement in a basic solution. Cadmium was plated on spring steel from a Cadalyte bath under the following conditions:

Cadalyte, grams/liter	125
Temperature, °F	77
Cathode current density, amperes/sq ft	25
Time, min	10

The bend values, after plating two specimens as above, were 67° and 55°. Two more were plated consecutively after Rochelle salts were added to the bath (100 grams/liter). All other conditions were the same. The bend values were 82° and 82°. The unplated stock did not fracture when bent up to 175°; this was the limit of the bending apparatus.

Experiments 40 and 41 of table 1 show that the catalytic (inhibition of hydrogen entry) power of hydroxide was poisoned by cyanide.

Experiments 45 to 55.- The same catalysts mentioned above were effective in lessening embrittlement during metal deposition. Table 2 contains the experimental conditions and results of their influence on embrittlement incurred during the zinc plating of spring steel. The inhibition was not pronounced, but it was significant in consideration of the extreme susceptibility of spring steel to embrittlement.

Remarks.- Citrate and tartrate are effective inhibitors of hydrogen entry from basic solutions. In acid solution, they are not effective unless converted to complex salts with aluminum or possibly other trivalent metals such as iron, chromium, cobalt, and so forth. Citrate and tartrate act the same in catalytically decomposing copper hydride. They do not catalyze the decomposition of that alloy in acid solution unless converted to complex salts with aluminum and so forth.

Oxidizing Agents as Inhibitors of Embrittlement Incurred during Pickling and Metal Deposition

Experiments 56 to 60.- Table 3 shows the ability of methylene blue to inhibit embrittlement during the cathodic pickling of steel. The table also gives the conditions of the experiments made. Table 4 shows the ability of the same dye to depolarize a metal cathode (experiment 60).

Experiment 61.- To demonstrate the inhibiting action of methylene blue toward hydrogen entry in plating baths, 0.2 gram per liter was added (very little dissolved) to a zinc-cyanide bath. The untreated steel gave a bend value of 175°. Steel plated with zinc with no addition of methylene blue gave bend values of 67°, 65°, 70°, and 65°. With the addition of methylene blue, the bend values were raised to 127° and 128°. The steel used was shim stock in panels 3 inches by 1/2 inch by 9 mils.

The zinc bath and plating conditions were as follows:

Zinc oxide (ZnO), grams/liter	52
Sodium cyanide (NaCN), grams/liter	93
Sodium hydroxide (NaOH), grams/liter	20
Cathode current density, amperes/sq ft	37
Temperature, °F	122
Anode	Two c.p. zinc sticks
Cathode	Steel (1/2 in. by 3 in. by 9 mils)
Plating time, min	5

One such oxidizing system combined catalysis (of the reaction $2H[M] \longrightarrow H_2 + 2M$, where M indicates a metal) and oxidation. The complex formed in solution of citric acid and ferric salts decomposed copper hydride very rapidly, even at pH values below 1. This decomposition very probably was primarily by oxidation, rather than catalysis, because the aluminum complex was not catalytically active at pH values below 1 but was very active at a pH of 4.6. Solution of copper to form a blue complex of Cu^{2+} was equally good evidence for the oxidation rather than catalytic decomposition of the hydride.

The following solution was used for pickling plain carbon steel:

Citric acid, grams	210
Ferric ammonium sulfate, grams	240
Water, liter	1

After operating the bath (100 ml) for 1 hour at 110 amperes per square foot, there was still no evidence of having reduced the iron. Hence, the bath could have been used indefinitely just as a bath containing the complex of aluminum sulfate and citric acid. The solutions were equally good as regards inhibition of embrittlement.

Experiment 62.- This experiment was designed to test an extreme case related to the ability of depolarizers to prevent embrittlement.

A thick slurry of manganese dioxide (MnO_2) in a 10-percent sulfuric-acid solution was used for the cathodic pickling of SAE 4130 steel. The steel was pickled at 110 amperes per square foot for 10 minutes at 80° F. After pickling, the steel specimen (Rockwell C value, 34) took a full 175° bend. When pickled at 220 amperes per square foot for 10 minutes at 80° F, it again took a full bend of 175° without cracking.

Without the oxidizing agent (MnO_2) in the acid, the bend values would have been 90° to 100° in the first case (110 amperes/sq ft) and even lower after pickling at 220 amperes per square foot.

Remarks.- The data in this section show that quinonoid dyestuffs and other oxidizing agents reduce embrittlement incurred during pickling. Such oxidizing agents can readily accept atomic hydrogen. Therefore, in close contact with a metal surface, they promote decomposition of the surface-formed hydrogen-metal alloy resulting from hydrogen entry before hydrogen can diffuse further into the metal; or those oxidizing agents take up the hydrogen before it can enter.

Oxidizing agents reduce the efficiency of the pickling process in terms of the amount of molecular hydrogen available for blasting scale from the work. This would not be a disadvantage for electrodeposition of metals. Furthermore, they are reduced in the process and must be

replenished unless they are air-oxidized. For these reasons, their activity is of interest chiefly as regards a study of the mechanism of the entry of hydrogen into metals.

Among organic compounds, oxidation commonly takes place by the removal of hydrogen, that is, dehydrogenation. Colloidal palladium, if added to aqueous solutions of many organic compounds, is responsible for the catalytic oxidation of the compounds and becomes charged with hydrogen in the process. Thus, palladium plays the part of a combined catalyst and hydrogen acceptor, forming palladium hydride.

Specimens of palladium charged with hydrogen can pass their hydrogen on to reducible substances such as methylene blue, the catalyst acting as an intermediate carrier of hydrogen. Furthermore, methylene blue is spontaneously reoxidized by atmospheric oxygen so it, as well as the palladium, can be alternately hydrogenated and dehydrogenated repeatedly if there is free access of air to the solution. Other dyes of the quinonoid type can replace methylene blue as hydrogen acceptors, but they are not equally capable of air oxidation (none are sensitive to reduction by molecular hydrogen).

Quinonoid dyes may be considered free radicals as well as oxidizing agents. Unlike the trichloromethyl radical, they are stable free radicals and promote loss of hydrogen from metals because of the irreversibility of their hydrogenation in the absence of air.

Catalytic Effects Related to Efficiency of Oxidizing Agents as Inhibitors of Embrittlement

Oxidizing agents are more or less effective in their ability to depolarize a metal cathode and slow down entry of hydrogen into the metal, depending on how the metal itself promotes or retards the reaction

$$2H[M] \rightleftarrows H_2 + 2M$$

The following experiments were designed to permit observation of the catalytic influence of the metal on the efficiency of the oxidizing agent. Its efficiency was based upon how fast it was reduced and how much it inhibited embrittlement.

Experiments 63 to 66.- An attempt to increase the inhibiting action of methylene blue by the addition of a catalyst for hydrogenation of the dye resulted in raising the bend value by 25°. The bath and test conditions were as follows:

Sulfuric acid, percent	10
Arsenic (As^{5+}), gram/liter	0.7
Methylene blue, grams/liter	5.0
Temperature, °F	82
Time, min	4
Cathode current density, amperes/sq ft	72
Anode	Platinum
Cathode	SAE 4130 steel heat-treated to a Rockwell C hardness of 33
Catalyst	$TiOSO_4$

When pickled under the above conditions without the catalyst, the bend value was 45°. With the titanium peroxysulfate ($TiOSO_4$) present and without agitation, the bend value was 57°, and, with agitation, it was 70°.

In order to determine whether Ti^{4+} salts would inhibit embrittlement in the absence of methylene blue, a solution was prepared by dissolving titanium in 33 percent sulfuric acid and oxidizing to the peroxy salt with three drops of 30 percent hydrogen peroxide. High-carbon steel was pickled in this solution at 80° F and 50 amperes per square foot. The bend value was 57°. In 33 percent sulfuric acid without the titanium salt, the bend value was 56°.

Experiment 67.- To study the effects of arsenic and palladium on the reduction of methylene blue by atomic hydrogen, a copper rod $\left(1\frac{1}{2}\text{- in. diam.}\right)$ was plated with palladium and used as a cathode in a solution of 0.02 gram per liter of methylene blue in 10 percent sulfuric acid. To prevent oxidation of the methylene blue by the oxygen from the anode, two cells were used, connected by a 10-percent sulfuric-acid bridge. Nitrogen was used to agitate the catholyte and to provide a nonoxidizing atmosphere.

At 35 amperes per square foot and 190° F, using the palladium-plated cathode, 15 minutes of plating were required to reduce the concentration of methylene blue by one-half. With a steel cathode under the same conditions, 7 minutes were required.

When arsenic (0.9 gram/liter) was present, using the palladium cathode, only 2 minutes were required to reduce the concentration to one-half, and the solution was entirely colorless in $5\frac{3}{4}$ minutes. With arsenic present, using a steel cathode of the same area, $5\frac{1}{2}$ minutes were required to reduce the concentration to one-half.

It may be seen from the results that the different metal-hydrogen alloys reduced a given depolarizer at different rates.

Experiment 68.- The effect of pickling inhibitors on the rate of reduction of methylene blue by atomic hydrogen at the copper cathode was studied by using the same apparatus. The pickling inhibitor tested was n-amylamine; it showed no effect on the rate of reduction of methylene blue. The conditions and bath used were as follows:

Sulfuric acid, percent	10
Methylene blue, gram/liter	0.05
Cathode	1/4-inch-diameter copper rod
Cathode current density, amperes/sq ft	35
Temperature, °F	82
Plating time, min	20

Agitation was by nitrogen. The methylene blue was reduced to one-sixth its original concentration with and without the addition of n-amylamine.

The effect of the pickling inhibitor was no more pronounced in changing the embrittlement caused by arsenic than in changing the rate of reduction of methylene blue. Steel (SAE 4130) was pickled cathodically at 110 amperes per square foot for 10 minutes at 200° F in 10 percent sulfuric acid containing arsenious oxide (0.09 gram/liter). The bend values were 33°, 31°, and 36°. When repeated after the addition of n-amylamine (2 percent by weight), the bend values were 26°, 30°, and 30°. The bend tests and the study of rate of reduction of the depolarizing dye indicate that pickling inhibitors of the amine type had little effect on hydrogen entry. This agrees with the result that they also did not affect the efficiency of reduction of methylene blue during the pickling process.

Remarks.- The data in this section are in accord with the proposed entry mechanism. Pickling inhibitors that do not readily take hydrogen from the surface-formed hydrogen-metal alloy of entry, or which do not take the hydrogen before it can enter, do not influence embrittlement one way or another.

Phase-Boundary Reactions Involving Free Radicals

The entry and exit of hydrogen into and from metals are equally influenced by the environment. The role of free radicals in these processes is important, because they are always present and are perpetuated by chain reactions with the solvent. For example, the uncharged hydroxide ion would be formed by chain reactions of free radicals in aqueous solutions.

The inhibitors of chain reactions involving free radicals include molecules which yield stabilized resonance systems, as for example, the quinonoid dyestuffs and similar heterocyclic compounds (e.g., methylene blue). Such compounds may also be classed as simple oxidizing agents and are discussed, as such, in another section of the report.

Free radicals are perpetuated, on the other hand, by compounds which form radicals of high energy content. Because of this difference in activity, all free radicals will not show the same activity toward hydrogen in metals and effect the same changes in permeability of a metal to hydrogen.

Carbon tetrachloride is typical of the class of compounds forming radicals of high energy content. The reactions,

$$Cl\cdot + CCl_4 \rightleftharpoons Cl\text{-}Cl + \cdot CCl_3$$

$$H\cdot + CCl_4 \rightleftharpoons H\text{-}Cl + \cdot CCl_3$$

illustrate, by their reversibility, that carbon tetrachloride does not tend to destroy hydrogen bound in atomic form. When carbon tetrachloride is in the medium supplying hydrogen to a metal, it should inhibit decomposition of metal hydrides and solid solutions of hydrogen in metals.

The object of these experiments was to determine whether such action would promote hydrogen entry and embrittlement and relate the phenomenon to the chemical behavior of hydrogen in metals.

Before describing the experiments, it is necessary to point out the fact that any reagent which will react with and remove one of the two products of the above equilibrium reaction with atomic hydrogen should make CCl_4 act as methylene blue or nitric oxide in preventing entry. These are examples of the stabilized free radicals which should prevent embrittlement and speed up decomposition of hydrogen alloys because they decompose hydrogen-metal alloy phases by their oxidizing action.

Experiments 69 and 70.- It is well-known that dry, crystalline potassium chloride has the property of poisoning the recombination of free radicals, including atomic hydrogen. Coatings of this material have been used on the interior of reaction vessels to make possible the study of homogeneous gas-phase reactions involving free radicals without interference from a simultaneous heterogeneous reaction on the walls of the vessels. Carbon tetrachloride, lead, and arsenic are known to poison similar reactions, though less effectively.

The object of these experiments was to determine what effect, if any, these substances would have on the rate of exit of hydrogen from metals.

Potassium-chloride solution was allowed to dry on one side of SAE 4130 steel hardened to a Rockwell C value of 33. The specimens were pickled on the opposite side for 10 minutes in 10 percent sulfuric acid at 80° F and 220 amperes per square foot. There was no indication of embrittlement; the steel withstood a full 175° bend. Without the dry salt on the back, the specimens broke at 45° to 50° bends.

With arsenic plated on the backs of cathodes, the bend values observed were 60° and 70°. With lead (approximately 1.4 mils thick), the bend values were 70° and 110°. All these tests confirmed the opinion that the rate of exit of hydrogen can be decreased by those three coatings and, thus, embrittlement can be reduced.

Furthermore, these results show that, unless hydrogen had left a metal by alloy decomposition, there might not have been enough concentration gradient from "entered" hydrogen at the surface as compared with the inside of the metal to cause diffusion of the hydrogen inward. This was an instance where the rifting of metals (see appendix A) was necessarily associated with the entry mechanism. Rifting and exit phenomena are both secondary effects which lead to changes in permeation by further hydrogen. By reducing the exit rate (and the amount of hydrogen which passes through the metal), it is likely that rifting and consequent increased permeability are likewise decreased.

Experiments 71 and 72.- The object of these experiments was to prove that the above reagents prevent escape of hydrogen from metals.

A palladium strip was cathodically charged with hydrogen, and the gas evolved from it under water over a 10-minute interval was 4.7 milliliters. When the palladium was heated to remove hydrogen and recharged and the gas was collected under dilute sulfuric acid containing As_2O_3, the gas evolved in 10 minutes was only 2.3 to 2.7 milliliters. Under carbon tetrachloride, only 0.2 milliliter was evolved in the 10 minutes. Even after 2 hours, only 0.6 milliliter was evolved. The same specimen gave off an additional 0.3 milliliter of hydrogen in only 10 minutes when it was wiped free of carbon tetrachloride and transferred to water.

The fact that hydrogen left palladium slower when the metal was under carbon tetrachloride than when it was under water substantiates the conclusion of experiments 69 and 70. The reason palladium was used should be explained. First, palladium can take up a large volume percent of hydrogen. Secondly, it is characteristic of palladium to release the hydrogen it contains rapidly. Hence, it is logical that the

rate of loss, if slowed down by "exit poisons" like carbon tetrachloride, could easily be detected.

Experiment 73.- Metals which have a high overpotential because the reaction

$$2H[M] \rightleftarrows H_2 + 2M$$

is slow should exhibit such a slow rate of loss of hydrogen that, unlike palladium, the rate would not be reduced by carbon tetrachloride. The object of this experiment was to determine whether the rate of loss of hydrogen from spring steel would be affected by carbon tetrachloride.

Five specimens of spring steel were pickled in 10 percent sulfuric acid at 110° F for 5 minutes. One was bent immediately after pickling (24° bend). Two were kept in air and bent after 50 minutes (46° and 43° bends). Two were kept in carbon tetrachloride and bent after 50 minutes (44° and 46° bends). The environment had no effect on the rate of loss of hydrogen, in apparent contradiction to the tests with palladium (71 and 72). It may be concluded, however, that there was no contradiction, because carbon tetrachloride was no better poison for the exit reaction

$$2H[M] \rightleftarrows H_2 + 2M$$

than the spring steel itself.

Experiment 74.- This experiment had the same objective as experiments 71 and 72, but the experimental conditions differed.

Two pieces of normalized SAE 4130 sheet steel were coated completely with Pyseal as a stop-off. One of the two had been previously coated on one side with a thin layer of dry, crystalline potassium chloride. A suspension of fine, powdery potassium chloride was prepared by adding a small volume of a saturated aqueous solution of the salt to a large volume of acetone. The suspension was poured on the steel and quickly evaporated to dryness.

On each specimen, a 1/4-inch-wide strip of the steel was exposed by removal of the Pyseal. This was done on the side opposite the potassium chloride on the specimen which had been treated with the salt.

Both specimens were pickled in 10 percent sulfuric acid at 6 amperes per square inch for the same time interval (not recorded). The Pyseal on the back of the specimen not coated with salt was blown up into large blisters. The back of the other specimen showed no evidence that hydrogen had been evolved at the back surface.

The conclusion is again that poisons for the reaction

$$2H[M] \rightleftarrows H_2 + 2M$$

retarded the rate of loss of hydrogen from the metal. The results show that the entry mechanism involved the formation of hydrogen-metal alloys such as hydrides (intermetallic compounds) and/or solid solutions.

Experiments 75 to 83.- The promoter activity of carbon tetrachloride is shown by the data of table 5.

The data also show that methylene blue, nitric oxide, and CCl_4, stabilized by the presence of iodide, inhibited embrittlement.

The pickling baths used in the tests are described below:

Bath A - 10-percent sulfuric-acid solution - 10 volumes of sulfuric acid (sp. gr., 1.84) to 90 volumes of water

Bath B - Bath A, dilute sulfuric acid, saturated with CCl_4

Bath C - Bath B after adding 5 percent potassium iodide (KI)

Bath D - Bath A, 10-percent solution of sulfuric acid, saturated with nitric-oxide gas (NO)

Experiment 84.- The hydrogen in cathodically charged palladium is obviously not inert toward carbon tetrachloride. The following experiment was designed to prove that the reaction

$$H\cdot + CCl_4 \rightleftarrows HCl + \cdot CCl_3$$

can take place at a cathode during pickling and result in increased embrittlement through prolonging the life of hydrogen alloys. A piece of palladium, which had been cathodically charged with hydrogen, was placed in an aqueous solution of silver nitrate saturated with carbon tetrachloride. A heavy cake of silver chloride rapidly formed on the surface of the metal, indicating that the above reaction was taking place and was being displaced to the right through reaction of a product (HCl) with silver ions in the solution.

Remarks.- It may be concluded from the data of table 5 that stable free radicals inhibit embrittlement of metals and that compounds forming unstable free radicals promote embrittlement when present in the

environment which is the source of the hydrogen. Moreover, it may be concluded that they act as described by virtue of their influence on the rate of decomposition of bound hydrogen in metals, that is, decomposition of hydrides and solid solutions into metal plus molecular hydrogen.

The conclusions agree with the following information taken from the general technical literature:

The gas, NO, is reduced by:

1. Atomic hydrogen, even at the temperature of liquid air

2. Nascent hydrogen from tin and hydrochloric acid

3. Hydrogen included in platinum

4. Nickel reduced from its hydroxide by hydrogen (colloidal nickel does not reduce it)

5. Freshly reduced gold, silver, and lead (the massive metals do not reduce it)

6. Hydrogen gas in the presence of tin, iron, or zinc (in the same way that quinonoid dyes are readily reduced by hydrogen in metals)

As opposed to nitric oxide and quinonoid dyes, a variety of organic liquids slow down the rate of loss of hydrogen from copper hydride.

Trichloroethylene, the common degreasing compound used to clean metals before electrochemical operations, was shown (reference 8) to undergo hydrogen-deuterium exchange. Similarly, there can be an exchange for hydrogen atoms. The extreme sensitivity of cathodic-reaction products to supposedly inert compounds is evident from this fact alone, as is the fact that any trichloroethylene entering a plating tank might be prone to cause embrittlement as carbon tetrachloride does.

A striking aspect of the conclusions to be drawn from this free-radical study is that they deny the validity of that phase of the "slip-plane-rift" theory related to the mechanism for the entry of hydrogen into steel. This theory relates to the conception that inclusion of hydrogen in metals is specifically connected with the presence or formation of rifts or opened structure in a metal. Smith (reference 9) extends the theory to explain (1) the inclusive inertness of metals after high-temperature annealing by a closing up of the structure of the metal and (2) the increased permeability in the presence of arsenic and similar impurities by an opening of structure by formation of arsenides and

other compounds. This cannot be reconciled with the ability of carbon tetrachloride to prevent escape of hydrogen from palladium and with the catalytic effects associated with CuH decomposition, especially in view of the fact that, by transferring the specimen from carbon tetrachloride to water, the gas evolution resumes. Such treatment can hardly be expected to close and open rifts in a metal any more than potassium chloride (KCl) on the back of steel could influence rift formation on the front pickled surface.

Envelope Protection of Metals Susceptible to Embrittlement by Metals Impermeable to Hydrogen

Experiment 85.- Complete envelope protection of SAE 4130 steel by lead plate (0.7 ml) and tin plate (0.2 and 1 mil) reduced embrittlement to the extent that full 175° bends were obtained after pickling cathodically at 122° F and 1 ampere per square centimeter, for 10 minutes. Unplated specimens broke at 45° to 50° under these conditions.

The lead was deposited from a nonembrittling fluoborate bath: 107 milliliters of lead fluoborate (50 percent) were diluted to 500 milliliters, and 20 milliliters of animal glue solution were added (40 grams/liter). The bath was operated at 80° F with lead (c.p.) anodes and at a cathode current density of 20 amperes per square foot.

Remarks.- Metals having little or no hydrogen solubility are known to be impermeable coatings preventing entry of hydrogen into the basis metals. This fact is not in contradiction to the entry mechanism proposed in this report. Surface formation of hydrides (intermetallic compounds) can occur without hydrogen penetration because, without some solubility, there can be no diffusion in from the surface.

DISCUSSION

Results

Several known methods of controlling the entry and exit of hydrogen in steel were correlated with the known chemical behavior of atomic and molecular hydrogen. Through this correlation, suitable reagents were found which increase or, for the first time, significantly decrease hydrogen permeability and embrittlement of steel during cathodic pickling operations in dilute sulfuric acid. This successful correlation was an important step toward arriving at the mechanism of hydrogen entry into steel. The same data showed that the diffusion of hydrogen in steel and the freedom of exit of hydrogen are also important in determining

the extent of embrittlement. Heretofore, the separate importance of entry and exit has not been clearly recognized and subjected to independent control. The phenomena are chemical and not mechanical. Entry is through the direct formation of metal hydrides (intermetallic compounds) or solid solutions of hydrogen in metal at the instant of hydrogen discharge. Exit is the decomposition of metal hydrides or of solid solutions of hydrogen in metal.

Entry first is possibly by solid solution. When the concentration becomes great enough (for a particular metal), there is a phase change to a hydride (an intermetallic compound). "Alloy" formation is accomplished throughout the metal because of the mobility of hydrogen atoms (or possibly protons).

The physical picture of the mechanism of hydrogen entry into metals is proposed as shown in figure 2. The mechanism for the entry of hydrogen into a metal is the same mechanism as that for the discharge of a metal ion on a different metal accompanied by alloy formation. In both cases, there is an excess energy requirement related to alloy formation. The problem is a particular part of the general problem of the pressure-temperature equilibrium of solids. Once formed, the hydrogen alloy decomposes E_x or is diminished in its hydrogen content by migration (D in fig. 2) of hydrogen atoms or protons at a rate proportional to the hydrogen-concentration gradient within the metal. Ultimately, the rate of the exit process on the other side (rate of alloy decomposition) affects this rate of diffusion. Environmental factors at the metal surface influence the exit process E_x as shown in figure 2, which illustrates that the rate of decomposition of hydrogen alloys is influenced (as any other chemical reaction) by catalysts and other reactants and that the rate of formation of the alloys is controlled by the conditions of reaction (temperature, concentration, particle size, pressure, voltage, electromagnetic radiation, and so forth).

The rate of accumulation of hydrogen in the metal is dependent on the relative speeds of entry, diffusion, and exit under whatever environmental conditions prevail.

An important showing of the work reported herein is that additives were found which reduce entry of hydrogen into hardened SAE 4130 and other steels during cathodic pickling and into spring steel during zinc and cadmium plating without lessening the apparent quality of the pickling or the plating. Also, if trichloroethylene (or other chlorinated hydrocarbons) enters a plating or pickling solution (as from a prior degreasing step), hydrogen embrittlement can be increased.

Newly Proposed Mechanism

The new mechanism proposed by figure 2 involves more than the process E_n. Also, the influence of the prevailing environment on E_n and E_x is important. The step E_n is based on considering that atomic hydrogen is a metal. The published literature supports the view that hydrogen behaves like a metal. (See reference 9.) Then, the process of entry E_n in figure 2 is simply one of forming a solid solution and/or an intermetallic compound. Showing that such an operation takes place with an element as mobile as hydrogen is experimentally difficult. However, there are analogies and experiments that can support the entry and exit (E_n and E_x) processes very clearly. Also some supporting evidence has been discussed in the literature and is presented in appendix A.

The principles that apply when gases combine with metals also apply to any case in which an alloy is raised to such a temperature that one of the constituents has an appreciable vapor pressure. For example, at temperatures above 932° F, the compositions of the phases of brass that may be kept at equilibrium depend upon the vapor pressure of zinc that is maintained. Thus, the modes of combination of a gas and a metal may be expressed in terms of a conventional phase diagram.

Therefore, the present thesis is that hydrogen, by forming alloys during chemical or electrochemical reactions at the metal surface, "plates into" the metal surface. The mechanism agrees with the universally accepted principle that gases "diffuse into a metal as single atoms." It also shows how they enter the metal, that is, solution or compound formation is essential to entry. Whether a hydrogen atom reacts with the metal or a proton is reduced, an alloy must be formed in the process, and the entry is accomplished.

Anything that prolongs the life of hydrogen in the "metallic" or alloyed state will cause an increased rate of accumulation of hydrogen in the metal. Accumulation is inhibited by environmental conditions which accelerate the chemical reaction of hydrogen alloys with other substances or the spontaneous decomposition of the alloys. These environmental factors are also shown in figure 2, because of their effects on the rate of entry and exit, according to the new mechanism.

Studies of, and experiments on, metal hydrides, the influence of such substances as arsenic, sulfur, phosphorus, carbon tetrachloride, and so forth on increasing the rate of accumulation of hydrogen in a metal, and the influence of inhibitors of hydrogen embrittlement support the mechanism for entry of hydrogen.

Battelle Memorial Institute
Columbus, Ohio, December 31, 1950

APPENDIX A

LITERATURE SURVEY

Other Proposals Related to Entry Mechanism

One proposal related to the entry mechanism is the concept that inclusion of hydrogen in metals is specifically connected with the presence or formation of rifts or opened structure in metals. This mechanism proposes that lattice defects are frequently dominant in determining the behavior of a given hydrogen-metal system. The rifting of metallic crystals or, in other words, the opening of enlarged interplanar spacings is related to inclusive permeability and capacity.

All the accumulated evidence supporting this mechanism is given by Smith (reference 9). Much of the evidence is directed toward proving that hydrogen is not held in solid solution (or as a hydride) in metals at lower temperatures. According to the rift mechanism, any phase transformation in a hydrogen alloy which is accompanied by an increase in the volume of the lattice produces a decrease of permeability and inclusive capacity and vice versa.

Even in the statement of the mechanism, it is apparent that a new phase has been formed and/or decomposed in a hydrogen alloy before the rifting shows its effects, which are then secondary to the entry into the pure metal.

Publications (e.g., reference 10) quoted by Smith as favoring the possibility that lattice intervals are disturbed by codeposition of hydrogen and chromium may be discounted by the work of Snavely (references 5 and 6) who has shown that direct hydride formation and subsequent decomposition is responsible for the structure of chromium plate.

The rift idea should, at most, be extended to the entry mechanism only to explain secondary effects associated with hydrogen entering and leaving hydrogen alloys. If a hydride or solid solution is formed as a part of the entry mechanism, any lattice distortion consequent to this entry should be considered secondary to this entry and to the entry of more hydrogen later.

The second mechanism for hydrogen entry into metals which has been found in the literature is that based on kinetic expressions for possible phase-boundary processes involved when hydrogen enters a metal. (See reference 11.) Such expressions account for the great discontinuities in hydrogen concentration at the surface of a metal. As a mechanism,

however, they must be accepted with some reserve, because fixing the nature of the rate-controlling process by noting the type of kinetic expression followed is inconclusive. Furthermore, as a mechanism, it is devoid of any notions as to the chemistry related to the entry of hydrogen into metals. Hence, it has limited value in predicting how hydrogen entry and hydrogen embrittlement may be controlled.

Evidence for Newly Proposed Mechanism Based on Earlier Literature

The literature concerning hydrogen overpotential on metals lends support to the hydrogen-entry mechanism proposed in this report. Hydrogen-overvoltage consideration, more than any other single factor, led to the concept that hydrogen enters a metal through solid solution or compound formation at the instant of discharge.

In general, a catalyst is responsible for lowering the energy of activation required for a reaction. Platinum, as a catalyst for reactions involving atomic hydrogen, has been said to "adsorb hydrogen atoms" with a heat of adsortion of approximately 53,000 calories per gram per atom. Thus,

$$H_2 = 2H\cdot \qquad \Delta H = 2 \times 52{,}089 \text{ cal/mole}$$

$$Pt + H\cdot = H[Pt] \qquad \Delta H = -53{,}000 \text{ cal/mole}$$

$$2Pt + H_2 = 2H[Pt] \qquad \Delta H = -2000 \text{ cal/mole}$$

The heat of dissociation of adsorbed hydrogen molecules is seen to be very low on platinum. This low energy accounts for the low hydrogen overpotential on platinum. Therefore, molecular hydrogen is not much more stable than the "hydride." The adsorbed hydrogen atoms are now viewed as being "in" the platinum as a surface intermetallic compound or a solid solution $\left(H[Pt] \text{ or } 2H[Pt]\right)$.

The platinum-hydrogen situation can be applied to cathodic discharge of hydrogen on metals in general. The sequence would be:

$$2M + 2H^+ + 2\epsilon = 2H\cdot[M]$$

$$2H\cdot[M] = H_2 + 2M$$

The net reaction, thus, is:

$$2H^+ + 2\epsilon = H_2$$

If hydrogen is soluble in a metal, then the instant $2H\cdot[M]$ is formed, hydrogen is in the metal and can diffuse further in by whatever mechanism is involved in solid diffusion of one metal in another.

If hydrogen is not soluble in the metal, it remains in an unstable surface $2H[M]$ condition available for immediate reaction with some other substance in the environment at, but outside, the metal surface and/or also forms molecular hydrogen.

The formation of a hydride has been experimentally demonstrated to be the rate-controlling step in the electrodeposition of hydrogen on a metal. Grube (reference 12) showed that, although AsH_3 acted as an inert gas in the presence of hydrogen gas in acid solution, it decomposed in basic solution and gave a reversible electrode of the type AsH_3, As, and H^+. In 1N and 0.1N sodium-hydroxide solutions, the decomposition potential of arsine corresponded to the overpotential of hydrogen on elementary arsenic in the same solutions. Therefore, in a basic solution, hydrogen evolution on an arsenic cathode must occur as follows:

$$As + 3H^+ + 3\epsilon \rightleftarrows AsH_3$$

$$AsH_3 \longrightarrow As + 1\tfrac{1}{2}\,H_2$$

Atomic hydrogen, as such, is not associated with the first process, but a hydride is. The base has catalyzed the second reaction to the extent that the first reaction is rate determining. Thus, the electrode potential can be expressed as

$$\epsilon = \epsilon_o + \frac{0.059}{3} \log \frac{C^3{}_{H^+}}{C_{AsH_3}}$$

where

ϵ_o standard electrode potential of half cell when each substance is in its standard state

C partial pressure in atmospheres for gases and activity of ionic species

It was 25 years later that Feitknecht and Warf (reference 2) demonstrated the catalytic decomposition of copper hydride by hydroxide ions.

Now, the present work, reported herein, has shown that CuH can undergo electrolytic-catalytic decomposition, just as has been described for arsine. When CuH is made cathodic in 10 percent sulfuric acid, it is converted to metallic copper. Apparently, when hydrogen is plated

on a copper-hydride cathode, the cathode film becomes basic enough to decompose the hydride.

A recent study on overpotential (reference 13) supports the hypothesis that the rate-determining step in the "over-all mechanism" occurs after the discharge of hydrogen and that the overpotential is due to the resulting stationary concentration of adsorbed atoms or radicals at the metal surface. The catalytic and electrochemical mechanisms fall under the same hypothesis. The former refers to surface combination to give molecular hydrogen; the latter refers to discharge and combination of an ion in solution with a surface-adsorbed atom, that is, the intermetallic alloy or solid solution of hydrogen.

Ultraviolet light was known to depolarize a variety of electrodes, and semiquantitative measurements of the photocurrent (i.e., the extra current required to return the electrode to its original potential) were made. Hillson and Rideal (reference 13) determined the quantum efficiency of the photoreaction.

The results of the study may be expressed by the equation

$$\log \gamma = \text{Constant} + \log i + (\beta h\nu/2.30\ kT)$$

where

$\beta = 1/30$

$h\nu$ energy of incident quanta

γ quantum efficiency

i polarizing current, amperes per square centimeter

The constant of the above equation was of the same order on all the metals studied, although the overpotentials and work functions differed considerably. At constant current density, the relation between $\log_e \gamma$ and $h\nu$ was linear but changed slope at 4.5 electron volts on platinum in an acid solution and, in an alkaline solution, at 4.3 electron volts on platinum, 4.5 on silver, and 3.5 on gold.

The same authors (reference 13) explained these phenomena as follows: In aqueous solution, the chemisorbed monolayer on a metal is normally oxygen atoms. Since the heat of adsorption of oxygen is usually much greater than that of hydrogen, the hydrogen is displaced.

At negative potentials, the chemical potential of the adsorbed hydrogen increases, corresponding to an increase in pressure by a factor of 3×10^3 for each tenth of a volt in excess of the reversible hydrogen potential, while the chemical potential of the oxygen is correspondingly decreased. The oxygen is displaced and is replaced by hydrogen. The high quantum efficiencies observed for the photoreaction at the more negative potentials show that an electrode, at which molecular hydrogen is being evolved at a sensible rate, is covered with a complete, or nearly complete, layer of chemisorbed hydrogen. The potential a at which the moelcular hydrogen is evolved (overpotential, $a + b \log i$) depends primarily on the potential required for the hydrogen to displace the chemisorbed oxygen and, hence, on the difference in the heats of adsorption of hydrogen and oxygen on the metal.

In the case of metals for which the heats of adsorption of hydrogen and oxygen are comparable, a considerable fraction of the electrode is covered with chemisorbed hydrogen so that hydrogen may be deposited at a sensible rate. Then, the metal can be used to measure the reversible hydrogen-electrode potential.

For metals with large differences in the heats of adsorption of the two gases, the difference in the ΔH values of the following reactions

$$M + H_2O = M\text{-}O + H_2$$

$$M + \frac{1}{2} H_2O = M\text{-}H + \frac{1}{4} O_2$$

can be taken as the voltage required (above reversible hydrogen potential) to replace chemisorbed oxygen by hydrogen.

The chemisorbed hydrogen of Hillson and Rideal, according to the present report, is the hydrogen that is in the metal by intermetallic-compound (hydride) or solid-solution formation M-H as proposed in the section "Results" of this report. This adsorbed hydrogen can be removed by the irreversible process associated with either the catalytic or electrochemical mechanism. Although hydrogen is known to diffuse into the bulk phase of many metals, it is unlikely that, under steady conditions, the process of diffusion is rapid enough to constitute a significant fraction of the over-all current, except possibly on palladium. Nevertheless, such diffusion can slow down attainment of a steady overpotential and is a sound basis for the newly proposed mechanism of hydrogen entry into metals.

The electrochemical mechanism for the evolution of hydrogen is

$$\epsilon + M\text{-}H + H_3O^+ \longrightarrow M\text{-}H^-\text{-}H^+ + H_2O \longrightarrow M + H_2 + H_2O$$

Thus, for metals which strongly adsorb oxygen, hydrogen evolution is possible only if the potential attains a relatively high cathodic value. Under these conditions, the H_3O^+ ions present in the solution will be strongly adsorbed onto the negative $[H \cdot M]$ surface.

Freshly prepared Raney nickel contains so much hydrogen that its formula is nearly that of an intermetallic compound, NiH_2. (See reference 14.) The electrochemical mechanism of the present report would predict that such nickel would act as a reversible hydrogen electrode, because all the adsorbed oxygen is replaced by hydrogen. Such is found to be the case, because Raney nickel has the same reducing potential as platinum black. Thus, Raney nickel is an "alloy" of hydrogen and nickel.

The well-documented mechanism of hydrogen overpotential has never before been correlated with hydrogen entry into metals. It is identical with the newly proposed mechanism for hydrogen entry into a metal through formation of a solid solution and/or an intermetallic compound (hydride) at the instant of discharge. In that instant, hydrogen does not appear as either a free atom or a molecule.

APPENDIX B

MEASUREMENT OF HYDROGEN EMBRITTLEMENT

This section describes the method for measuring the extent of hydrogen embrittlement as a test of the processes under study for hydrogen entry and exit.

Apparatus

The machine for measuring hydrogen embrittlement was constructed similar to that described by Zapffe and Haslem (reference 15) for measuring embrittlement as a function of the angle at which breaking occurs during a single bend made at constant speed (see fig. 3). The driver was a synchronous 60-rpm motor, geared down to give a bending rate of 4.4° per second.

Choice and Preparation of Suitable Specimens

It was desirable to use SAE 4340 steel for the embrittlement tests, but the smallest diameter rod available (3/4 in.) could not be drawn to suitable diameter for use in the bending apparatus. Therefore, in lieu of SAE 4340, SAE 4130 was selected. Sheet steel (3/32 in. thick) was machined to a thickness of 0.068 inch and cut into 3-inch by 1/4-inch specimens. They were heat-treated in a reducing atmosphere to a Rockwell C hardness of 34. They were then pickled at 86° F and 110 amperes per square foot for 10 minutes, rinsed, dried, and placed under mercury for analysis within 1 minute after pickling.

Determination of Reliability of Constant-Rate Bend Test as an Indication of Relative Hydrogen Content

Experiments 86 to 91 were conducted to determine the reliability of the bend test as an indication of relative hydrogen content among specimens of SAE 4130 steel which were identical except as regards their hydrogen content.

Except for the method of analysis, the experimental conditions and results are given in table 6. Hydrogen content was determined by hot extraction of the gas, the volume being measured under reduced pressure. The method is accurate to ± 0.3 part per million for residual hydrogen in

steel. Hydrogen evolved from the steel stored under mercury can be measured with an accuracy of only ±3 parts per million. The poor correlation can be corrected by developing a method of measuring the evolved gas with the same accuracy as the residual gas in the metal.

It may be concluded that the bend test gives no indication of relative hydrogen content of small specimens of steel.

REFERENCES

1. Wagner, W.: Procedure for Preparing Films of Copper Adhering Particularly to Glass and Porcelain. Ceramic Abstracts, vol. 18, 1939, p. 6.

2. Feitknecht, W., and Warf, James C.: Zur Kenntnis des Kupferhydrids, insbesondere der Kinetic des Zerfalls, Helvetica Chim. Acta, vol. 33, 1950, pp. 613-639.

3. Rhines, F. N., and Anderson, Wm. A.: Hydrogen Embrittlement of Pure Copper and of Dilute Copper Alloys by Alternate Oxidation and Reduction. Metals Technology, vol. 7, no. 7, Oct. 1940, pp. 1-11.

4. Mantell, C. L.: Industrial Electrochemistry. McGraw-Hill Book Co., Inc., 1940.

5. Snavely, C. A.: Theory for the Mechanism of Chromium Plating; a Theory for the Physical Characteristics of Chromium Plate. Trans. Electrochem. Soc., vol. 92, 1947, pp. 537-577.

6. Zapffe, Carl A., and Haslem, M. Eleanor: Measurement of Embrittlement during Chromium and Cadmium Electroplating and the Nature of Recovery of Plated Articles. Trans. Am. Soc. Metals, vol. 39, 1947, pp. 241-258; discussion by Cloyd A. Snavely, pp. 258-260.

7. Mueller, H., and Bradley, A. J.: CCXVII. Copper Hydride and Its Crystal Structure. Jour. Chem. Soc., pt. IV, 1926, pp. 1669-1673.

8. Leitch, L. C., and Bernstein, H. J.: Deuterium Exchange in Trichlorethylene. Canadian Jour. Res., sec. B, vol. 28, no. 1, Jan. 1950, pp. 35-36.

9. Smith, Donald P.: Hydrogen in Metals. The Univ. of Chicago Press, 1948.

10. Hume-Rothery, William, and Wyllie, Malcolm R. J.: The Structure of Electro-deposited Chromium. Prox. Roy. Soc. (London), ser. A, vol. 181, no. A987, July 28, 1943, pp. 331-344; also, The Structure of Electro-deposited Chromium. A Correction. Proc. Roy. Soc. (London), ser. A, vol. 182, no. A991, June 16, 1944, p. 415.

11. Barrer, R.M.: Diffusion in and through Solids. Cambridge Univ. Press (London), 1941.

12. Grube, G., and Kleber, H.: The Overvoltage of Hydrogen at Arsenic Cathode and the Electromotive Behavior of Arsine. Zeitschr. Elektrochemie, vol. 30, 1924, pp. 517-523.

13. Hillson, P. J., and Rideal, E. K.: On Overpotential and Photovoltaic Process at Polarized Electrodes. Proc. Roy. Soc. (London), ser. A, vol. 199, no. 1058, Nov. 7, 1949, pp. 295-310.

14. Schroeter, R.: Reduction with Raney Nickel Catalysts. Translated and revised by I. Salminen in Newer Methods of Preparative Organic Chemistry, Interscience Publishers, Inc. (New York), 1948, pp. 61-101.

15. Zapffe, Carl A., and Haslem, M. Eleanor: A Test for Hydrogen Embrittlement and Its Application to 17 Per Cent Chromium, 1 Per Cent Carbon Stainless-Steel Wire. Tech. Pub. No. 1954, Am. Inst. Min. and Met. Eng., 1946.

TABLE 1.- CATALYTIC INHIBITION OF HYDROGEN EMBRITTLEMENT

Experiment	Pickling bath (1)	Temperature (°F)	Current density (amperes/sq ft)	Time (min)	Angle of fracture (deg)
SAE 4130 steel (Rockwell C value, 49)					
25	(2)	---	---	---	>175
26	A	90	100	5	67, 72
27	B	90	100	5	>175, >175
28	C	90	100	5	>175,130, >175
Plain carbon steel					
29	(2)	---	---	---	>175
30	A	88	110	5	50
31	A	85	110	5	58, 61, 56
32	D	88	110	5	>175
33	D	85	220	5	>175, >175
Spring steel					
34	(2)	---	---	---	>175
35	A	190	36	10	45
36	B	190	36	10	75
37	E	190	36	10	87
Steel shim stock (3)					
38	E	180	63	10	Not blistered nor brittle
39	A	80	63	10	Blistered and brittle
40	B	80	200	10	Not blistered nor brittle
41	B + cyanide	80	200	10	Blistered and brittle

[1]See text for bath composition.

[2]Specimen was not pickled.

[3]Highly susceptible to blister formation during cathodic pickling.

TABLE 2.- EFFECT OF BATH ADDITIVES ON EMBRITTLEMENT INCURRED

DURING ZINC PLATING OF SPRING STEEL

[Plating conditions: Cathode current density, 25 amperes/sq ft; bath temperature, 86° F; plating time, 20 min. Plating bath: $ZnSO_4 \cdot 7H_2O$, 240 grams/liter; NH_4Cl, 20 grams/liter; volume, 500 ml]

Experiment	Additive to plating bath	Angle of fracture (deg)	Remarks
45	None	69	Bath pH adjusted to 4
46	None	68	Bath pH adjusted to 4
47	12.5 grams of $Al_2(SO_4)_3 \cdot 18H_2O$	58	pH not adjusted after addition
48	12.5 grams of $Al_2(SO_4)_3 \cdot 18H_2O$	60	pH not adjusted after addition
49	7.2 grams of Rochelle salt plus 12.5 grams of $Al_2(SO_4)_3 \cdot 18H_2O$	87	pH not adjusted after addition
50	7.2 grams of Rochelle salt plus 12.5 grams of $Al_2(SO_4)_3 \cdot 18H_2O$	93	pH not adjusted after addition
51	28.6 grams of Rochelle salt plus 50 grams of $Al_2(SO_4)_3 \cdot 18H_2O$	53	pH not adjusted after addition
52	28.6 grams of Rochelle salt plus 50 grams of $Al_2(SO_4)_3 \cdot 18H_2O$	57	pH not adjusted after addition
53	28.6 grams of Rochelle salt plus 50 grams of $Al_2(SO_4)_3 \cdot 18H_2O$	75	Bath pH returned to 4
54	28.6 grams of Rochelle salt plus 50 grams of $Al_2(SO_4)_3 \cdot 18H_2O$	87	Bath pH returned to 4
55	28.6 grams of Rochelle salt plus 50 grams of $Al_2(SO_4)_3 \cdot 18H_2O$	76	Bath pH returned to 4

TABLE 3.- ESSENTIAL DATA ON INHIBITING EFFECT OF

METHYLENE BLUE

[Acid bath - 10 percent H_2SO_4 containing 0.0924 gram/liter of As_2O_3; pickling conditions - 110 amperes/sq ft for 10 min at 195° F]

Experiment	Concentration of methylene blue (percent)	Remarks	Angle of fracture (deg)
56	None	SAE 4130 steel	45, 47
57	0.1	SAE 4130 steel	53, 60
58	1.0	SAE 4130 steel	59, 59
59	1.0	With palladium flash plate on steel	61, 62

NACA

TABLE 4.- POTENTIAL OF CATHODE AGAINST SATURATED CALOMEL ELECTRODE IN PRESENCE AND ABSENCE OF DEPOLARIZING AGENT (EXPERIMENT 60)

[Cathode current density, 1 ma/cm^2; temperature, 80° F]

Metal as cathode	Potential (volts)					
	2N H_2SO_4		2N H_2SO_4 + 0.1 percent MB[1]		2N H_2SO_4 + 0.1 percent MB[1] + 0.062 gram of Ti^{4+}/100 ml	
	No agitation	With agitation	No agitation	With agitation	No agitation	With agitation
Bi	0.984	0.660	0.713	0.248	0.686	0.105
Cd	1.014	.850	.920	.821	.904	.728
Zn	1.077	1.001	.930	.919	.956	.925
Pb	1.209	.941	.966	.534	.954	.514
Cu	.865	.815	.684	.442	.720	.517
Pt	.372	.357	.344	.306	.356	.344
Electrolytic Fe	.584	.538	.541	.496	.535	.498

[1]0.1 gram of methylene blue (MB) per liter of 2N sulfuric acid.

TABLE 5.- EMBRITTLEMENT AS AFFECTED BY PHASE-BOUNDARY REACTIONS INVOLVING FREE RADICALS

Experiment	Pickling bath (1)	Temperature (°F)	Current density (amperes/sq ft)	Time (min)	Angle of fracture (deg)
SAE 4130 steel (Rockwell C value, 34)					
75	(2)	---	---	---	>175
76	A	80	110	10	90 to 100
77	B	80	110	10	33, 50, 40
78	C	80	110	10	>175
79	D	80	110	10	>175
SAE 4130 steel (Rockwell C value, 49)					
80	(2)	---	---	---	>175
81	A	90	100	5	67, 72
82	B	90	100	5	57, 57
83	C	90	100	5	130, 82, 78

[1]See text for bath composition.

[2]Specimen was not pickled.

TABLE 6.- TEST OF RELIABILITY OF CONSTANT-RATE BEND TEST

AS AN INDICATION OF HYDROGEN CONTENT

Experiment	Pickling bath	Hydrogen content (ppm)
86	10-percent sulfuric-acid solution	0.7
87	10-percent sulfuric-acid solution	.4
88	10 percent H_2SO_4 saturated with CCl_4	Lost
89	10 percent H_2SO_4 saturated with CCl_4	.6
90	Citric acid monohydrate, 10 grams; aluminum sulfate, 10 grams; water, 90 ml	.7
91	Citric acid monohydrate, 10 grams; aluminum sulfate, 10 grams; water, 90 ml	1.5

(a) 10 percent sulfuric acid.

(b) 10 percent sulfuric acid plus 0.09 gram per liter of arsenious oxide (As_2O_3).

Figure 1.- Bubble formation at same current density during electrolytic pickling in two different baths.

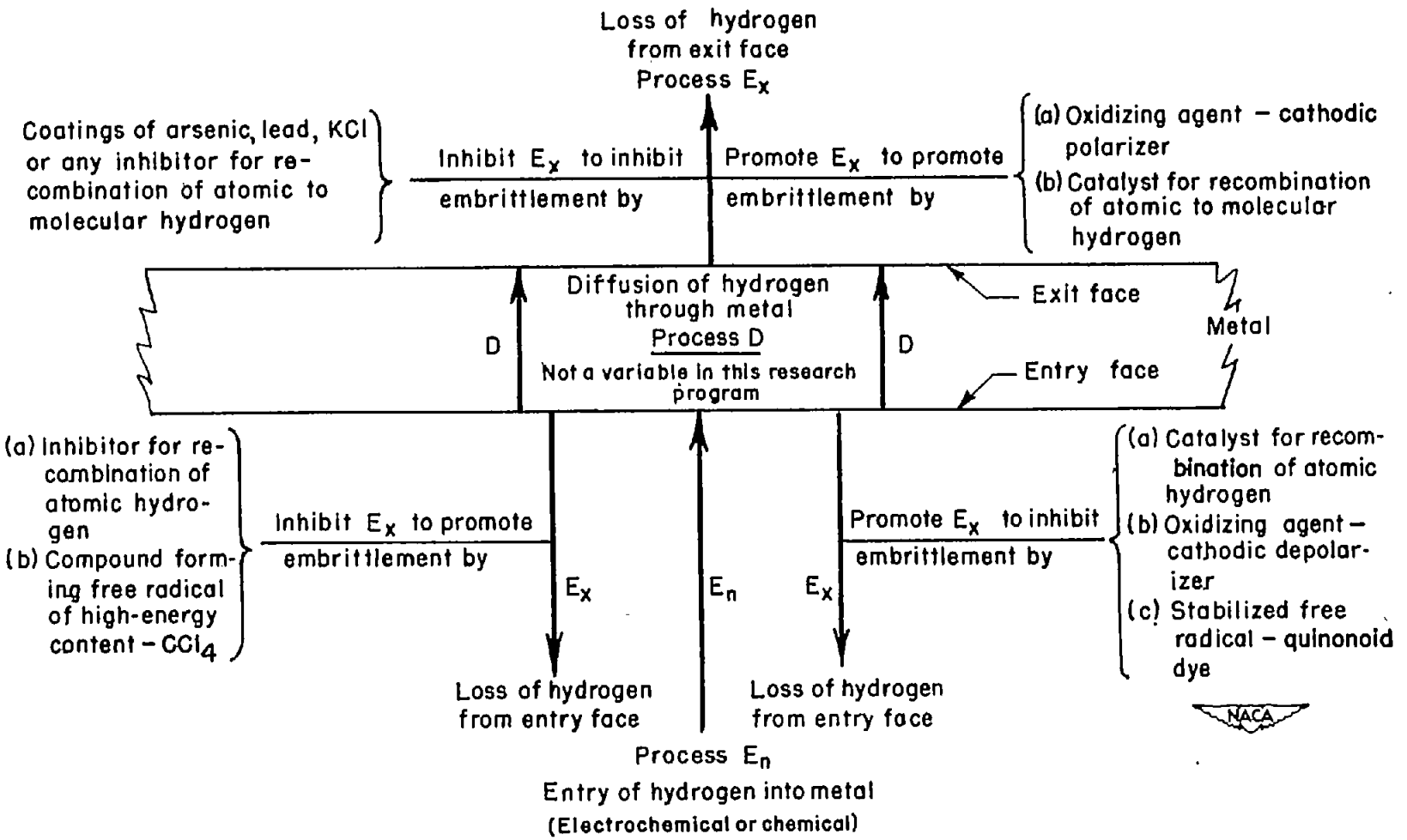

Figure 2.- Regulatory influences on permeability of metal to hydrogen during electrochemical processing.

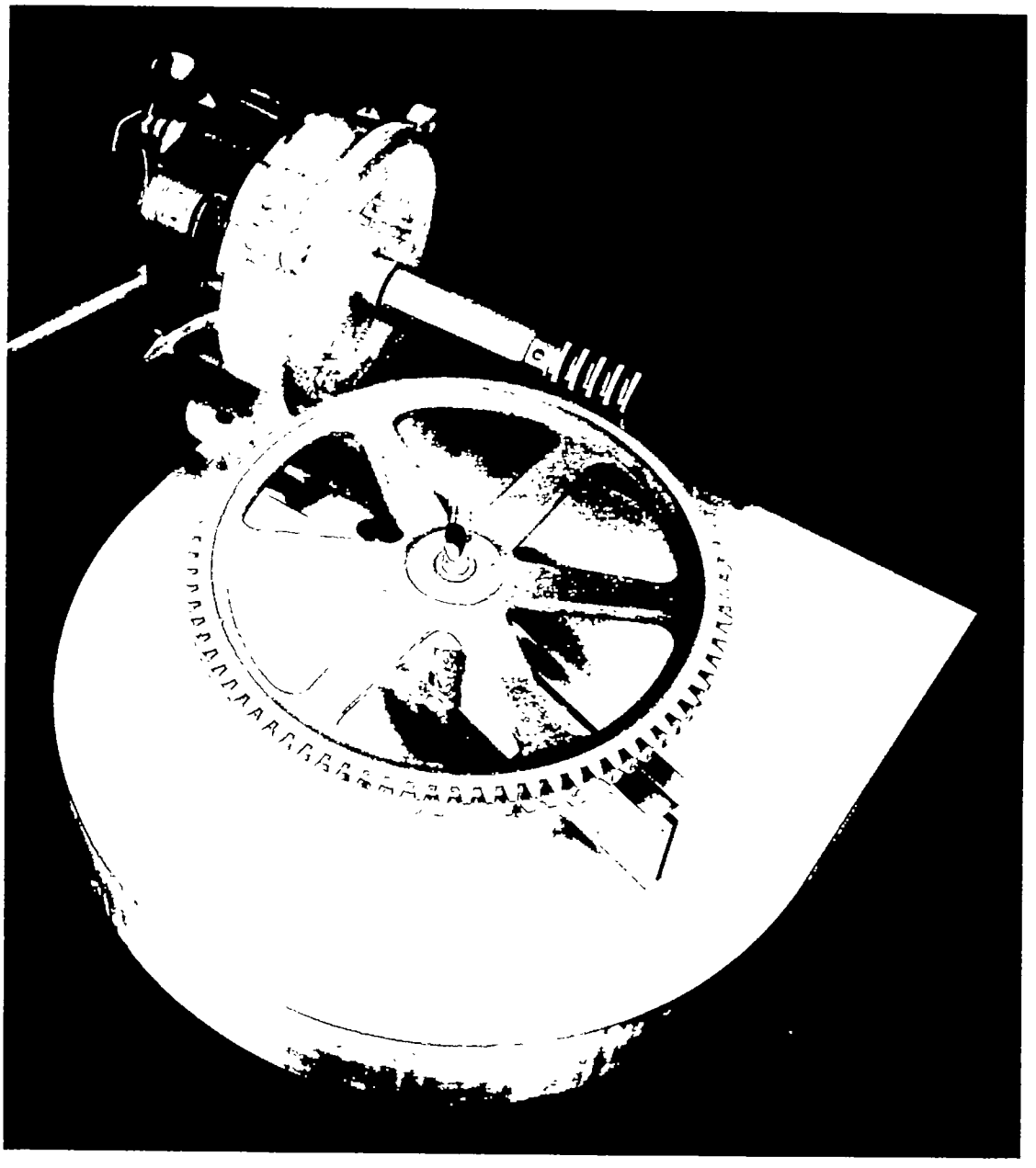

Figure 3.- Apparatus for measuring hydrogen embrittlement in steel by means of a constant-rate single bend.

NACA-Langley - 12-31-53 - 120