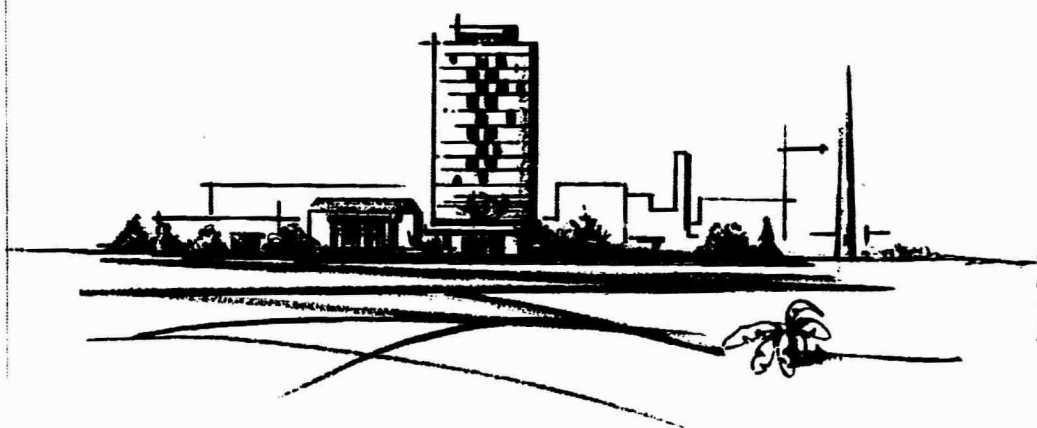
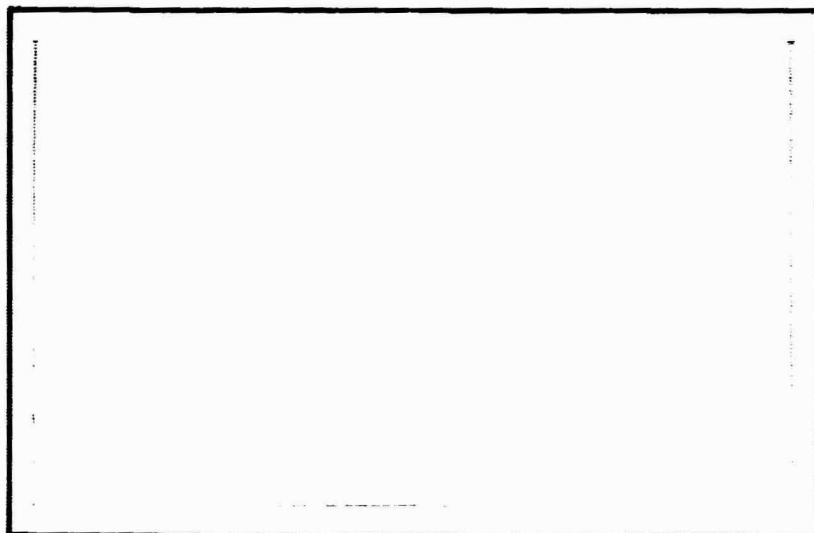


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## BATTELLE MEMORIAL INSTITUTE

### COLUMBUS LABORATORIES



**SPECIAL REPORT**

on

**A REVIEW OF THE LITERATURE ON PICKLING  
INHIBITORS AND CADMIUM ELECTROPLATING  
PROCESSES TO MINIMIZE HYDROGEN ABSORP-  
TION BY ULTRAHIGH-STRENGTH STEELS**

to

**NATIONAL AERONAUTICS AND  
SPACE ADMINISTRATION  
GEORGE C. MARSHALL  
SPACE FLIGHT CENTER**

**November 15, 1967**

by

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**Ferrous Metallurgy Division  
Process and Physical Metallurgy Department**

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# A REVIEW OF THE LITERATURE ON PICKLING INHIBITORS AND CADMIUM ELECTROPLATING PROCESSES TO MINIMIZE HYDROGEN ABSORPTION BY ULTRAHIGH-STRENGTH STEELS

by

T. P. Groeneveld, E. E. Fletcher, and A. R. Elsea

## INTRODUCTION

As the strength levels and design-stress requirements of high-strength steels have been increased to meet the demands of the aircraft and aerospace industries, the problem of hydrogen-induced delayed brittle failure, or hydrogen-stress cracking, of parts fabricated from these steels has become of great concern. The primary reason for this problem is that most of these high-strength steels have to be protected from corrosion in their service environments. The preferred method of providing this protection is cadmium electroplating. However, the application of electrodeposited coatings to solve corrosion problems, or to provide other desirable surface qualities, can make the part susceptible to failure by hydrogen-stress cracking because, frequently, hydrogen is introduced during the cleaning, pickling, and electroplating operations.

As a result of hydrogen-stress-cracking failures attributed to hydrogen introduced during bright-cadmium electroplating, the Air Force placed restrictions on the use of cadmium electroplating on certain steels having tensile strengths greater than 220,000 psi. Thus, it was necessary for manufacturers to resort to other methods of providing corrosion protection that were inferior to bright-cadmium electroplates in the protection provided. Consequently, many studies of electroplating processes, particularly cadmium electroplating, have been conducted to determine whether one or more processes could be used for electroplating ultrahigh-strength steels without the likelihood of encountering hydrogen-stress-cracking failures.

These studies showed that most ultrahigh-strength steels were embrittled to various degrees by virtually all of the common electroplating processes, including cadmium, chromium, zinc, tin, nickel, lead, copper, and silver. These earlier studies also showed that the amount of hydrogen entering steel specimens during certain electroplating processes may be as great as that introduced during severe cathodic charging and that more hydrogen sometimes was introduced during pickling or cathodic cleaning prior to electroplating than during the actual plating operation. As a result of these findings, some work has been expended in evaluating the hydrogen-embrittling tendencies of preplating cleaning and pickling processes, particularly on the effectiveness of inhibitors in minimizing hydrogen absorption during acid pickling. In addition, these studies showed that the sustained-load tensile test employing notched bars was the most sensitive method for evaluating the embrittling tendencies of cleaning and electroplating processes.

Because of numerous confusing and conflicting statements contained in the technical literature concerning the hydrogen-embrittling tendencies of various cleaning, pickling, and electroplating processes and concerning the susceptibilities to hydrogen-stress cracking of various high-strength alloys, a program was undertaken at Battelle in 1965 to evaluate various processes and materials of interest to NASA. As part of each of the two

previous terms of Contract No. NAS 8-20029, "A Study of Hydrogen Embrittlement of Various Alloys", literature and industrial surveys were conducted. The first survey constituted a review of the literature on the phenomenon of hydrogen-stress cracking and the embrittling tendencies of conventional cleaning, pickling, and electroplating processes. In the report on this survey, the results of numerous investigations into this problem area were included along with data on the effectiveness of various hydrogen-embrittlement relief treatments.<sup>(1)</sup> The report on the literature and industrial survey conducted during the second term of this contract presented information on reportedly low-hydrogen-embrittling and nonhydrogen-embrittling cleaning, pickling, and electroplating processes and on hydrogen-embrittlement relief treatments.<sup>(2)</sup>

This report describes the results of a literature and industrial survey of the available information on the effectiveness of inhibitors for reducing hydrogen absorption by steels during acid pickling and on additional low-hydrogen-embrittling and nonhydrogen-embrittling cadmium-electroplating processes. No attempt has been made to repeat the information on pickling inhibitors and cadmium-electroplating processes presented in the previous reports. However, it was found desirable to include some reference to work described previously so as to provide necessary background information, to make desirable comparisons, and to be more complete in the discussions of certain processes.

The primary purpose in conducting the present survey was to obtain information to aid in the selection of pickling inhibitors and cadmium-electroplating processes to be studied in the present term of the research program.

#### THE EFFECTIVENESS OF INHIBITORS FOR REDUCING HYDROGEN ABSORPTION BY STEELS AS A RESULT OF ACID PICKLING

During processing and fabrication, metals acquire scale and oxide coatings as well as other surface contaminants. Various cleaning processes are used to remove these surface contaminants. The commonly used cleaning processes include abrasive cleaning (such as grit blasting and tumbling), salt-bath descaling, alkaline descaling, and acid pickling for the removal of surface oxides; and solvent cleaning, vapor degreasing, emulsion cleaning, and alkaline cleaning for the removal of oil, grease, and dirt. Selection of the cleaning process is influenced primarily by the type of surface contamination to be removed, the required degree of cleanliness, and the cost. Several references are available which describe these various cleaning processes in detail;<sup>(3, 4, 5, 6)</sup> hence, except for pickling, these cleaning processes will not be considered further.

Acid pickling is used to:

- (1) Remove scale completely by either the acid treatment alone or after the scale has been conditioned in a caustic bath.
- (2) Remove contaminated or damaged surface metal
- (3) Remove oxide film

- (4) Activate the metal surface for electroplating by removal of superficial oxide or passivating films
- (5) Passivate the metal surface to provide greater corrosion resistance.

Sulfuric and hydrochloric acid solutions are most commonly used to pickle carbon and low-alloy steels. However, the use of hot, concentrated solutions of these acids as a single pickling treatment for complete removal of scale is declining, and use of these acids at lower concentrations and lower temperatures as a supplementary treatment following abrasive cleaning or salt-bath descaling is gaining favor.

Sulfuric acid pickling baths generally are used at concentrations of 5 to 15 percent by volume of commercial acid (98 percent acid by weight) in water at temperatures of 140 to 180 F for 5 to 45 minutes for removal of mill scale and rust. The pickling rate increases proportionately as the concentration is increased up to 25 percent. Above 25 percent the pickling rate goes up more slowly. Also, increasing the temperature increases the pickling rate; between 70 and 210 F, the pickling rate doubles for each 15 to 20 F temperature rise.

Hydrochloric acid pickling baths most frequently are used at room temperature at concentrations of 25 to 50 percent by volume of commercial acid (30 to 32 percent acid by weight) in water. Hydrochloric acid tends to leave less pickle smut than does sulfuric acid. Therefore, in some operations, a short, final treatment in this acid (10 to 25 percent by volume for 2 to 5 minutes) follows sulfuric acid pickling. Hydrochloric acid has a more rapid pickling action on the base metal which results in an increased tendency for pitting.

Phosphoric acid also is used to remove rust and scale, often where other special properties are required. The most significant of these are avoidance of pitting and reduction of re-rusting. For heavy pickling, this acid usually is used at concentrations of 15 to 40 percent by weight at 120 to 180 F; light pickling with this acid is done at concentrations of 15 to 30 percent by weight at room temperature to 140 F. Smut is produced to a lesser extent with phosphoric acid than with sulfuric acid but to a greater extent than with hydrochloric acid. However, its lower pickling rate and its greater cost limit the use of phosphoric acid.

A considerable amount of pickling is carried out in which gross oxide (such as mill scale, heat-treat scale, or heavy rust) is not present. For applications such as enameling, tinning, galvanizing, or electroplating, it is necessary to remove light oxide to provide a clean surface which enhances adherence of the coating to the base steel. The metal surface is said to be activated when this type of pickling has been carried out. Treatments of this type are not limited to carbon or alloy steels; they are important for stainless steels or nickel-base alloys that are passive due to the presence of extremely coherent oxide films on the surface.

Activation pickling prior to electroplating may consist of short-time dips in 0.5 to 10 percent sulfuric acid, 1 to 25 percent hydrochloric acid, or 2 to 25 percent phosphoric acid. Other possible activation treatments include 2 to 10 percent acetic acid, 1 to 10 percent citric acid, or the other organic acids that are good sequestrants for metal ions. Fluoboric acid dips often are used prior to electroplating in a fluoborate bath.



Certain additions can be made to pickling baths to increase the pickling rate, but these additions do not accelerate pickling to the same extent for all steels. Other methods used to accelerate pickling are the uses of electrolytic pickling or ultrasonic agitation of the pickling bath. Cathodic pickling is much faster than nonelectrolytic pickling or anodic pickling. However, the dangers of hydrogen embrittlement increase considerably when cathodic pickling is used.

The use of ultrasonic agitation during pickling has been reported by several investigators not only to increase the pickling rate but also to reduce hydrogen embrittlement slightly. (7, 8, 9) However, others<sup>(10)</sup> have reported that ultrasonic agitation increased hydrogen embrittlement during acid pickling. Thus, the value of ultrasonic agitation for reducing hydrogen embrittlement in steels during acid pickling is questionable.

The objective during acid pickling is to remove the scale with a minimum attack on the base metal. However, some attack on the base metal apparently is required because the reaction between the acid and metal forms hydrogen gas, the evolution of which helps to flake off the scale and provide agitation. In addition, hydrogen is presumed by some to reduce magnetic iron oxide to a form that is more easily removed<sup>(6)</sup>. At the same time, excessive reaction with the metal is not desired, because this consumes more acid, creates fumes, enhances hydrogen embrittlement, produces smut, causes pitting and reduction in surface quality, and may remove enough metal to affect dimensional tolerances.

The fact that pickling in acid solutions can result in considerable hydrogen pickup by the steel and subsequent embrittlement was discussed in the reports of the literature and industrial surveys conducted during previous terms of this contract. (1, 2)

The method most frequently used to reduce problems related to metal attack and hydrogen liberation during acid pickling is to add inhibitors to the pickling bath. An inhibitor may be defined as a material that reduces or stops the action of the acid on the base steel while allowing the reaction on the scale and oxides to continue.

Inhibitors may be classified on the basis of their action in a pickling bath, as follows:<sup>(11)</sup>

- (1) Organic compounds of the type that are unsaturated, and can take up nascent hydrogen as fast as it is formed, or organic compounds that are reduced by the nascent hydrogen with formation of some other compound that holds the hydrogen in chemical combination
- (2) Organic compounds that deposit colloidal or organic films
- (3) Inorganic compounds that deposit metallic films.

The organic inhibitors also may be classified on the basis of their source:<sup>(6)</sup>

- (1) Nitrogen- and sulfur-bearing materials occurring naturally in such products as glue, beer-fermentation dregs, and flour
- (2) Nitrogenous coal-tar-derived chemicals such as still residues, or more refined chemicals like quinaldine and substituted pyridines

- (3) Synthetic sulfur- and/or nitrogen-bearing chemicals like dibutyl thiourea, ditolyl thiourea, and hexamethylenetetramine.

The first group is of more interest from a historical viewpoint, although they are still used. (6, 11) A large number of proprietary formulations have been developed to obtain maximum inhibition of attack on metal with the fewest undesirable residues. In addition, many of these proprietary inhibitors contain foam-banquet-generating materials to keep fuming to a minimum and to provide some cleaning and wetting-out action.

The literature contains many references that report the effectiveness of numerous inhibitors for reducing metal loss (corrosion rate), hydrogen evolution, and acid consumption. In addition, several of these references discuss the action by which the various substances provide inhibition and discuss the general considerations of the use of inhibitors in acid pickling solutions. (11, 12, 13, 14, 15, 16) Uhlig has pointed out that the successful use of inhibitors frequently requires considerable knowledge of their action and a thorough understanding of the corrosion process in the system under consideration. (12) Substances that may successfully decrease the rate of attack on a metal or virtually nullify it in one environment may stimulate attack in another. In still other environments, the inhibitor may decrease the overall rate of attack but may bring about an increase in the intensity of attack at restricted anodic sites, leading to pitting and rapid perforation.

Evans, in describing the use of inhibitors to minimize hydrogen embrittlement, pointed out that, if reducing metal loss, hydrogen evolution, and acid consumption were the only objectives in using an inhibitor, any substance that obstructs any one of the several essential steps of the corrosion process could be used. However, to be effective in reducing hydrogen embrittlement, an inhibitor not only must reduce the total metal corrosion, which is equivalent to reducing the total amount of hydrogen produced, but also particularly, must reduce that fraction of the hydrogen that enters the metal and causes either blistering or cracking.

The majority of the work reported in the literature on the effect of inhibitors in reducing hydrogen absorption by steels during acid pickling has been done on plain-carbon or low-alloy structural-type steels in which gross hydrogen absorption during acid pickling can result in problems such as formation of blisters or cracking during subsequent fabrication, or blistering of coatings applied after pickling. Very little information was available on the effectiveness of inhibitors for eliminating or reducing embrittlement in ultrahigh-strength steels as a result of acid pickling.

Investigators at the United States Steel Corporation have conducted several studies on the effectiveness of various inhibitors for reducing hydrogen absorption during pickling in sulfuric and/or hydrochloric acid. One of these investigations<sup>(17)</sup> evaluated the influence of arsenic, a promoter of hydrogen absorption during cathodic charging, on the pickling rate and hydrogen absorption by low-carbon steel (0.064 percent C, 0.33 percent Mn) pickled in 2N sulfuric acid (9.26 percent by weight) at 38 C (100 F). Specimens of the steel were pickled for times of 8, 15, 30, and 60 minutes in prepared solutions containing additions of arsenic (as arsenic trioxide) up to 1 gram/liter. The pickling rate was determined by the weight loss of the specimen, and the hydrogen contents of the specimens were determined by the warm-extraction method.

The results of this study are presented in Table 1. The addition of 1 milligram/liter of arsenic to the 2N sulfuric acid significantly increased the pickling rate at 38 C

(100 F) over that of the arsenic-free acid, but additions of arsenic above 4 milligrams/liter inhibited the solution of the steel in the acid. The addition of up to 4 milligrams/liter of arsenic to this acid did not significantly alter the quantity of hydrogen absorbed by the steel during pickling as compared with the amount absorbed by the steel during immersion in arsenic-free acid. For additions of 8 milligrams/liter or more arsenic, the additions inhibited hydrogen absorption, with the degree of inhibition increasing with increasing arsenic concentration up to about 62 milligrams/liter, after which the amount of hydrogen absorbed was essentially constant regardless of the amount of arsenic added or of pickling time.

TABLE 1. INFLUENCE OF ARSENIC ADDITIONS TO 2N SULFURIC ACID ON THE PICKLING RATE OF AND HYDROGEN ABSORPTION BY LOW-CARBON STEEL AT 38°C (100 F)<sup>(17)</sup>

Arsenic Concentration in 2N Sulfuric Acid, mg/liter	Weight Loss, mg, for Indi- cated Immersion Times, min				Hydrogen Absorbed, cc per 100 g, for Indicated Immersion			
					Times, min			
	8	15	30	60	8	15	30	60
0	1.8	3.0	5.7	12.4	9.1	10.0	11.5	12.0
1	3.0	6.0	14.3	28.9	10.8	10.2	(a)	11.0
4	1.5	1.8	6.3	15.2	7.5	9.7	10.5	12.5
8	0.6	1.0	1.2	1.8	6.2	3.9	3.5	3.8
10	0.4	0.6	0.5	1.8	1.6	2.6	2.3	3.1
16	0.4	0.3	0.8	1.2	0.9	1.4	1.8	1.8
31	0.5	0.4	0.6	0.8	0.4	0.5	0.7	0.8
62	0.1	0.0	0.1	0.2	0.3	0.4	0.5	0.3
125	0.0	0.2	0.0	0.1	0.2	0.3	0.3	0.4
250	0.1	0.0	0.0	0.0	0.2	0.2	0.3	0.3
500	0.0	0.0	0.1	0.0	0.2	0.2	0.2	0.3
1000	0.0	0.0	(a)	0.0	0.3	0.2	(a)	0.2

(a) Not determined.

The inhibiting effect of arsenic on corrosion in acids has been attributed to the high hydrogen overvoltage of arsenic deposited on the cathodic areas of the metal surface. It has been suggested that the reason for the lack of protection against hydrogen embrittlement and actual promotion of hydrogen absorption during cathodic pickling is the simultaneous electrolytic deposition of hydrogen with arsenic, which prevents the building up of a coherent protective film of arsenic over the normally cathodic areas on the metal surface.

Hudson and Riedy studied the effectiveness of 16 water-soluble acetylenic compounds and 2 commercial inhibitors used in 2N sulfuric acid at temperatures of 100 and 180 F. The inhibiting effectiveness of these compounds was determined by measuring the weight loss and amount of hydrogen absorbed (warm-extraction method) by a low-carbon steel (0.022 percent C, 0.09 percent Mn) immersed for either 4 or 24 hours in solutions containing 0.05, 0.2, 0.4, and 0.8M additions of the compounds. The results of this study are summarized in Table 2.<sup>(18)</sup>



TABLE 2. EFFECTIVENESS OF PICKLING INHIBITORS IN 2N SULFURIC ACID AT 100 AND AT 180 F FOR 4-HOUR IMMERSION TIME(18)

Inhibitor	Inhibitor Concentration	Weight Loss, mg/cm <sup>2</sup>		Percent Inhibition		Hydrogen Absorbed, cc/100 g		Percent Limitation of Hydrogen Absorption	
		100 F	180 F	100 F	180 F	100 F	180 F	100 F	180 F
1-Propyn-3-ol	0.05M	0.4	11.7	98	95	1.0	3.1	88	86
1-Pentyn-3-ol	0.05M	0.2	2.3	99	99	1.0	1.2	88	95
1-Hexyn-3-ol	0.05M	0.2	3.2	99	99	1.2	0.3	85	99
4-Methyl-1-pentyn-3-ol	0.05M	0.2	4.9	99	98	0.9	0.5	89	98
1-Ethynylcyclohexan-1-ol	0.05M	0.4	1.9	98	99	0.7	0.3	92	99.9
2-Butyn-1, 4-diol	0.05M	0.4	7.0	98	97	1.4	3.1	83	86
3, 6-Dimethyl-4-octyn-3, 6-diol	0.05M	0.6	164.4	97	24	0.9	19.5	89	12
3-Methyl-1-pentyn-3-ol	0.05M	0.4	114.7	98	47	0.7	16.1	92	27
Inhibitor A	0.25 volume percent	0.2	0.3	99	99.9	1.3	5.6	84	75
Inhibitor B	0.25 volume percent	0.2	1.4	99	99.4	2.4	14.6	71	34
Uninhibited acid	--	21.1	216.5	0	0	8.3	22.1	0	0

Six of the acetylenic alcohols and two of the acetylenic diols were similar to the two commercial proprietary inhibitors in their ability to retard the dissolution of steel in acid. Most of the acetylenic compounds were as good as, or better than, the better of the two commercial proprietary inhibitors in limiting hydrogen absorption by the steel. In addition, most of the acetylenic inhibitors that were effective at 100 F also were effective at 180 F, while the commercial inhibitors were not nearly so effective in limiting hydrogen absorption at the higher temperature as they were at 100 F (see Table 2).

In a more recent study, Hudson and Warning evaluated the effectiveness of 49 organic compounds as inhibitors in both hydrochloric and sulfuric acid solutions during pickling of low-carbon steel (0.022 percent C, 0.14 percent Mn).<sup>(19)</sup> The compounds were arbitrarily listed in the following groups:

- (1) Nonheterocyclic compounds of nitrogen
- (2) Heterocyclic compounds of nitrogen
  - a. Pyrroles and condensed pyrroles
  - b. Pyridine, quinoline, and related compounds
- (3) Organic sulfur compounds
- (4) Organic compounds that do not contain nitrogen or sulfur.

Steel specimens were immersed for 4 hours at 100 F in 2N hydrochloric acid and sulfuric acid solutions containing the compound being evaluated. Solid compounds were used at 0.1 weight percent, and liquid compounds were used at 0.1 volume percent concentration. All solutions were tested when freshly made to avoid possible aging effects in the solution. The weight loss for the steel after 4 hours' immersion in uninhibited 2N hydrochloric acid at 100 F was 3.5 mg/cm<sup>2</sup> and in 2N sulfuric acid was 7.6 mg/cm<sup>2</sup>. The effectiveness of the various organic compounds in preventing dissolution of the steel was compared on the basis of the percent inhibition, I, defined by

$$I = \frac{(\text{Percentage change in weight, uninhibited acid}) - (\text{Percentage change in weight, inhibited acid})}{(\text{Percentage change in weight, uninhibited acid})} \times 100,$$

where the percentage change in weight is the change in weight divided by the initial weight of the respective samples times 100.

The hydrogen content of the steel after pickling was determined by the warm-extraction method. The relative effectiveness of each inhibitor in limiting hydrogen absorption was designated percent limitation of hydrogen absorption (L) and was computed according to the equation:

$$L = \frac{(C_{H_2, \text{ uninhibited acid}} - C_{H_2, \text{ inhibited acid}})}{C_{H_2, \text{ uninhibited acid}}} \times 100.$$

The hydrogen concentrations in the steel after 4 hours immersion at 100 F in uninhibited 2N hydrochloric acid and uninhibited 2N sulfuric acid were 4.5 and 6.6 cc/100 g, respectively.

The results of this investigation are presented in Table 3. For the low-carbon steel samples pickled for 4 hours in 2N hydrochloric acid at 100 F, the average I and L values of the 49 organic compounds tested were 64 and 47, respectively. For the pickling treatments in 2N H<sub>2</sub>SO<sub>4</sub>, the I and L values of the 49 compounds were 55 and 30, respectively.

TABLE 3. EFFECTIVENESS OF ORGANIC COMPOUNDS AS INHIBITORS  
IN 2N HCl AND H<sub>2</sub>SO<sub>4</sub> SOLUTIONS DURING PICKLING OF  
LOW-CARBON STEEL AT 100 F FOR 4 HOURS<sup>(19)</sup>

Compound	Percent Inhibition, I		Percent Limitation of Hydrogen Absorption, L	
	HCl	H <sub>2</sub> SO <sub>4</sub>	HCl	H <sub>2</sub> SO <sub>4</sub>
None	0	0	0	0
<u>A. Nonheterocyclic Compounds of Nitrogen</u>				
3-(N, N-Diethylamine)-1-propyne	91	90	84	85
n-Dodecylamine	97	65	98	16
Di-n-dodecylamine	34	28	-18	-21
Tridodecylamine	51	45	24	-10
Ethomeen C/12	94	92	96	82
Aniline	3	17	-11	-21
Cyclohexylamine	49	51	36	40
p-Toluidine	29	20	11	2
$\alpha$ -Naphthylamine	43	4	24	9
<u>B. Heterocyclic Nitrogen Compounds</u>				
Pyrrole	91	88	87	87
3-Pyrroline	61	20	49	0
Pyrrolidine	57	41	42	15
1-Methylpyrrole	89	86	82	79
2, 5-Dimethylpyrrole	91	80	87	65
Indole	97	97	93	90
Indoline	91	84	87	81
2-Methylindole	80	45	71	38
3-Methylindole	14	8	4	3
2, 5-Dimethylindole	66	12	44	6
Carbazole	11	-1	2	-25
Pyridine	23	36	13	16
Nicotinic acid	71	53	56	18
4-Picolene	40	53	33	12
2, 4-Lutidine	63	28	56	-2
Quinoline	74	43	60	22
Quinoline ethiodide	91	97	96	91
Isoquinolene	80	51	67	34
Quinaldine	80	62	67	34
7-Methylquinolene	80	61	76	38
8-Methylquinolene	71	53	62	32
2, 6-Dimethylquinolene	86	79	84	56
Pyrimidene	71	66	71	25
Pyrazine	63	63	73	65
Piperazine	54	8	42	-10
Melamine	37	18	20	-7
Cyanuric Chloride	29	46	16	-6
Hexamethylenetetramine	91	87	84	79

TABLE 3. (Continued)

Compound	Percent Inhibition, I		Percent Limitation of Hydrogen Absorption, L	
	HCl	H <sub>2</sub> SO <sub>4</sub>	HCl	H <sub>2</sub> SO <sub>4</sub>
<u>D. Organic Sulfur Compounds</u>				
Thiourea	20	87	-167	-66
1,3 Di-n-butyl-2-thiourea	94	97	64	85
Thiophene	34	4	-31	-41
Benzothiophene	34	25	13	4
Thiazole	49	22	-16	-50
Benzothiazole	94	93	62	68
S-Trithiane	83	58	33	-9
<u>E. Organic Compounds that do not Contain Nitrogen or Sulfur</u>				
Formaldehyde	69	72	71	60
Benzaldehyde	51	74	36	66
1-Hexyn-3-ol	97	99	89	90
2-Butyn-1,4-diol	91	95	82	88
Propiolic acid	77	83	78	74

The number of effective inhibitors for hydrochloric acid was considerably higher than the number of effective inhibitors for sulfuric acid. Many compounds were effective in both acids. Only 6 materials were more effective in sulfuric acid than in hydrochloric acid. In general, the ability of an inhibitor to limit hydrogen absorption during pickling paralleled its ability to limit metal dissolution. Some sulfur compounds with good corrosion-inhibiting characteristics acted as promoters for hydrogen absorption (negative value of L) so that the amount of hydrogen absorbed was greater than that absorbed during pickling in uninhibited acid. Similar results have been obtained in other investigations using sulfur-bearing compounds as inhibitors, notably thiourea and related compounds. (20, 21) Such behavior has been attributed to decomposition of the compound to form  $H_2S$  either by the temperature of the pickling bath or by some cathodic reaction that takes place during pickling.

This study also showed that, in certain analogous series of compounds, the inhibitor effectiveness decreased with an increase in the degree of saturation of the compound and tended to be poorer when substituent groups were added to the ring structure.

In a subsequent study, Hudson and Warning evaluated the effectiveness of sodium halides used alone or with organic compounds as inhibitors for use in pickling low-carbon steel in sulfuric acid solutions and the ability of such mixtures to limit hydrogen absorption by the steel during pickling. (20) The organic compounds studied were the same as those described previously (see Table 3).

Steel specimens were immersed at 200 F for 4 hours in 2N sulfuric acid solutions containing the inhibitor materials of interest. The sodium halides were evaluated at 0.01, 0.1, 0.5, and 1.0M concentrations in the 2N sulfuric acid. The organic compounds were evaluated without and with 0.05M sodium chloride; liquid compounds were used at a concentration of 0.1 percent by volume and solid compounds were used at a concentration of 0.1 percent by weight. A limited number of experiments were conducted at 100 F. From weight-loss measurements and from determinations of hydrogen content by the warm-extraction method, I and L values were calculated using the relationships described previously. The weight loss of this steel when pickled for 4 hours in uninhibited 2N sulfuric acid at 200 F and 100 F was 175 mg/cm<sup>2</sup> and 13 mg/cm<sup>2</sup>, respectively. The corresponding hydrogen concentrations were 8.6 and 4.8 cm<sup>3</sup>/100 g, respectively.

The effectiveness of the sodium halide salts as inhibitors in 2N sulfuric acid at 200 F is shown in Table 4. At all concentrations, sodium iodide was the most effective sodium halide salt for reducing both weight loss and hydrogen absorption. For sodium fluoride, the percent inhibition increased as concentration increased from 0.1 to 1.0M. For sodium chloride, bromide, and iodide, the percent inhibition increased to a maximum and then decreased with further increases in concentration. The limitation of hydrogen absorption by the halide additions was inferior to that of many inhibitors previously investigated by these techniques (see Table 3). (19) Similar results were obtained by Russian investigators studying the effect of halide ions on the dissolution rate of iron and steel in sulfuric acid. (22) They attributed the inhibiting effect of halide ions in sulfuric acid to displacement of one or more active sulfate ions from the surface of the metal by the halide ions. In accordance with this explanation, the inhibiting effect of halide ions is displayed only when their concentration is below a critical value; beyond this point, an increase in concentration is accompanied by a weakening of the inhibiting effect, or a faster dissolution of the steel, than is found for sulfuric acid without any additions. Others have attributed the inhibiting effect of halide ions to the formation of a monomolecular iron halide film that passivates the surface.

TABLE 4. EFFECTIVENESS OF SODIUM HALIDES AS INHIBITORS IN 2N SULFURIC ACID DURING PICKLING OF LOW-CARBON STEEL AT 200 F FOR 4 HOURS<sup>(20)</sup>

Halide	Concentration of Halide		Weight Loss, mg/cm <sup>2</sup>	Percent Inhibition, I	Amount of Hydrogen Absorbed, cm <sup>3</sup> /100 g	Percent Limitation of Hydrogen Absorption, L
	Molarity	Grams per Liter				
None	0	0	175	0	8.6	0
NaF	0.01	0.42	140	20	5.6	34
NaF	0.10	4.2	156	11	7.0	18
NaF	0.50	21	125	28	5.3	38
NaF	1.0	42	91	48	5.7	33
NaCl	0.01	0.58	168	4	7.2	15
NaCl	0.10	5.8	155	11	5.7	34
NaCl	0.50	29	137	22	5.0	42
NaCl	1.0	58	154	12	5.3	37
NaBr	0.01	1	158	10	6.0	30
NaBr	0.10	10	126	28	5.9	31
NaBr	0.50	51	70	60	3.6	58
NaBr	1.0	102	104	41	2.8	67
NaI	0.01	1.5	31	82	3.4	60
NaI	0.10	15	6	97	1.8	79
NaI	0.50	75	33	81	3.0	65
NaI	1.0	150	59	66	2.0	77

The effects of 0.05M NaCl additions to the 2N sulfuric acid solutions containing organic inhibitors are shown in Table 5.<sup>(20)</sup> This addition of 0.05M NaCl resulted in a significant improvement in the I value (that is, greater inhibition of metal attack) for 35 of the 49 organic compounds. With NaCl, 21 of the compounds had I values of 50 or more, whereas without NaCl only 8 had I values of 50 or more. The L values of 35 of the compounds were significantly improved by the NaCl addition; that is NaCl tended to limit or reduce hydrogen absorption by the steel. With NaCl, 19 compounds had L values of 50 or more, whereas without NaCl only 6 had L values of 50 or more. Since NaBr and NaI were shown to be more effective than NaCl when used alone, it would be expected that NaBr and NaI additions to the acid baths containing organic inhibitors would have even more pronounced beneficial effects.

Although L values cannot be predicted with certainty from the I values, there was a trend for relatively high L values to be associated with high I values. An exception to this relationship was evident with many of the organic sulfur compounds, which acted as hydrogen-absorption accelerators. This behavior may be attributed to partial decomposition of the compounds to form hydrogen sulfide, which is known to accelerate hydrogen entry into steel.

Many of the compounds which were rated as poor inhibitors at 200 F in this study have been reported to be effective in tests performed at lower temperatures.<sup>(19)</sup> Therefore, some of these organic compounds with and without NaCl additions were evaluated at 100 F. The results of these tests are presented in Table 6. In all cases, the addition of 0.05M NaCl improved the inhibitor effectiveness of the compounds studied at this lower



TABLE 5. EFFECTIVENESS OF ORGANIC COMPOUNDS AS INHIBITORS IN 2N SULFURIC ACID SOLUTIONS WITH AND WITHOUT 0.05M SODIUM CHLORIDE DURING PICKLING OF LOW-CARBON STEEL AT 200 F FOR 4 HOURS<sup>(20)</sup>

Compound	Concentration	Percent Inhibition, I		Percent Limitation of Hydrogen Absorption, L	
		Without NaCl	With NaCl	Without NaCl	With NaCl
None	--	0	44	0	0
<u>A. Nonheterocyclic Compounds of Nitrogen</u>					
3-(N, N-Diethylamine)-1-propyne	0.1 volume percent	20	50	19	36
n-Dodecylamine	0.1 volume percent	2	68	29	70
Di-n-dodecylamine	0.1 weight percent	41	78	-33	61
Tridodecylamine	0.1 volume percent	28	70	-21	70
Ethomeen C/12	0.1 volume percent	57	96	71	87
Aniline	0.1 volume percent	12	20	26	31
Cyclohexylamine	0.1 volume percent	16	13	36	36
p-Toluidine	0.1 weight percent	18	10	34	40
$\alpha$ -Naphthylamine	0.1 weight percent	5	23	26	39
<u>B. Heterocyclic Nitrogen Compounds</u>					
Pyrrole	0.1 volume percent	61	97	77	84
3-Pyrroline (dihydropyrrole)	0.1 volume percent	42	86	46	72
Pyrrolidine (tetrahydropyrrole)	0.1 volume percent	8	17	19	42
1-Methylpyrrole	0.1 volume percent	60	98	76	89
2,5-Dimethylpyrrole	0.1 volume percent	50	89	61	74
Indole	0.1 weight percent	51	92	74	87
Indoline	0.1 volume percent	18	83	42	75
2-Methylindole	0.1 weight percent	18	53	39	61
3-Methylindole (skatole)	0.1 weight percent	29	24	4	15
2,5-Dimethylindole	0.1 weight percent	19	33	34	49
Carbazole	0.1 weight percent	19	5	46	28
Pyridine	0.1 volume percent	13	11	27	21
4-Picoline	0.1 volume percent	11	9	42	35
2,4-Lutidine	0.1 volume percent	7	12	33	37
Nicotinic acid	0.1 weight percent	3	23	26	35
Quinoline	0.1 volume percent	19	31	35	48
Quinoline ethiodide	0.1 weight percent	64	79	4	68
Isoquinoline	0.1 weight percent	3	23	-6	26
Quinaldine	0.1 weight percent	25	29	35	45
7-Methylquinoline	0.1 weight percent	34	39	44	58
8-Methylquinoline	0.1 weight percent	26	33	48	53
2,6-Dimethylquinolene	0.1 weight percent	13	33	19	56
Pyrimidine	0.1 volume percent	34	87	40	68
Pyrazine	0.1 weight percent	35	65	55	46
Piperazine	0.1 weight percent	1	17	22	36
Melamine	0.1 weight percent	18	1	34	25
Cyanuric chloride	0.1 weight percent	11	10	33	32
Hexamethylenetetramine	0.1 weight percent	6	40	37	57
<u>C. Organic Sulfur Compounds</u>					
Thiourea	0.1 weight percent	85	82	-115	-122
1,3-Di-n-butyl-2-thiourea	0.1 weight percent	99	99	5	-13
Thiophene	0.1 volume percent	14	16	39	35
Benzothiophene	0.1 volume percent	15	16	35	34
Thiazole	0.1 volume percent	23	24	-11	-19

TABLE 5. (Continued)

Compound	Concentration	Percent Inhibition		Percent Limitation of Hydrogen Absorption	
		Without NaCl	With NaCl	Without NaCl	With NaCl
C. Organic Sulfur Compounds (Continued)					
Benzothiazole	0.1 volume percent	47	62	-61	-150
S-Trithiane	0.1 weight percent	33	89	-8	45
D. Organic Compounds Containing No Nitrogen or Sulfur					
Formaldehyde	0.1 volume percent	16	38	44	56
Benzaldehyde	0.1 volume percent	0	13	24	38
1-Hydroxy-3-ol	0.1 volume percent	30	65	38	57
2-Butyn-1,4-diol	0.1 weight percent	44	91	37	34
Propiolic acid	0.1 volume percent	21	20	39	46



temperature. Except for s-Trithiane, which, relative to uninhibited acid, was more effective at 200 F than at 100 F, the performance of these selected formulations was better at 100 F than at 200 F.

TABLE 6. EFFECTIVENESS OF SELECTED ORGANIC COMPOUNDS AS INHIBITORS IN 2N SULFURIC ACID SOLUTIONS WITH AND WITHOUT 0.05M SODIUM CHLORIDE DURING PICKLING AT 100 F FOR 4 HOURS<sup>(20)</sup>

Compound	Concentration	Percent Inhibition, I		Percent Limitation of Hydrogen Absorption, L	
		Without NaCl	With NaCl	Without NaCl	With NaCl
Pyridine	0.1 volume percent	35	65	17	14
Quinoline	0.1 volume percent	43	79	22	29
Indole	0.1 weight percent	98	99.5	90	95
p-Toluidene	0.1 weight percent	19	49	1	4
Hexamethylenetetramine	0.1 weight percent	86	95	80	84
s-Trithiane	0.1 weight percent	58	72	-9	-10
Formaldehyde	0.1 volume percent	72	91	61	66
1-Hexyn-3-ol	0.1 volume percent	99	99.5	90	96
None		0	44	0	0

Little information on the effectiveness of inhibitors for reducing hydrogen absorption by high-strength steels during acid pickling was obtained during this review of the literature. The information that was obtained was generally lacking in either hydrogen absorption data or delayed-failure data.

Russian investigators studied the influence of organic inhibitors on the cracking of high-strength steels during acid pickling.<sup>(23)</sup> The steels used were 30KhGSNA (0.30C, 1.15 Mn, 1.05 Si, 1.05 Cr, 1.60 Ni) and an experimental steel of the 30KhGSNA-type with an increased carbon content (0.41 C). The 30KhGSNA steel was heat treated to the 170 kg/mm<sup>2</sup> (242,000 psi) strength level, and the experimental steel was heat treated to the 210 kg/mm<sup>2</sup> (299,000 psi) strength level. The specimens were tested by stressing them in bending such that the tensile stresses at the outer fiber were equal to 145 kg/mm<sup>2</sup> (210,000 psi) and then immersing them in sulfuric or hydrochloric acid solutions containing the inhibitors under evaluation. The time required for the appearance of the first crack was measured and was used as the criterion for evaluation of the relative effectiveness of the inhibitors.

The results of this study are presented in Table 7. Most of the amines studied had little effect on the cracking tendency of 30KhGSNA steel in the sulfuric acid and hydrochloric acid solutions. Exceptions were urotropin, quinoline plus potassium iodide, and a proprietary inhibitor BA-6. The urotropin and BA-6 were more effective in the hydrochloric acid solutions than in the sulfuric acid solutions. In addition, it was shown that the efficiency of the inhibitors increased with their concentration in the range of 5 to 50 grams per liter, and with decreasing acid concentration. As shown in Table 8, aging of the hydrochloric acid-urotropin solution increased the inhibiting efficiency of the urotropin against cracking of the high-strength experimental steel.

TABLE 7. EFFECT OF INHIBITORS ON THE CORROSION CRACKING OF 30 KhGSA STEEL IN  $H_2SO_4$  AND  $HCl$ <sup>(23)</sup>

Compound	Concentration, g/liter	Time to Cracking, minutes			
		20 percent $H_2SO_4$		15 percent $HCl$	
		Minium	Average	Minium	Average
None	--	4	5	3	4
<b>A. Organic Inhibitors</b>					
Dimethylamine	10	7	7.3	--	--
Diethylamine	10	5	5.3	--	--
Diethylamine	50	5	9	--	--
Dibutylamine	50	14	45	--	--
Dimethylaniline	50	25	132	--	--
Diethylaniline	10	14	19	--	--
Diethylaniline	110	13	71	--	--
Hexamethylenediamine	50	8	11	--	--
Hexamethylenetetramine (urotropin)	10	19	104	--	--
Hexamethylenetetramine (urotropin)	50	26	323	300	>1400
Benzylamine	50	46	118	16	46
Monoethanolamine	10	5	7	--	--
Monoethanolamine	50	8	8.3	11	11.5
Triethanol	10	6	14	--	--
Triethanol	50	19	26	--	--
Thiocarbamide (thiourea)	10	9	16	10	18
Thiocarbamide (thiourea)	50	21	29	22	28
Phenylhydrazine (hydrochloric)	10	6	7.3	--	--
Quinoline	50	23	94	24	42
Pyridine	50	9	16	--	--
Quinoline + potassium iodide	16	>1600	--	--	--
Quinoline + potassium iodide	50	>1600	--	--	--
<b>B. Russian Proprietary Inhibitors</b>					
4M	1.5	26	36	--	--
4M	10	18	116	--	--
PB-5	10	20	64	70	78
PB-8	10	13	50	15	18
PB-8	50	--	--	19	58
BA-6	50	20	160	145	>1400
I-1-A	50	74	120	15	61
Catapin	50	63	72	14	30

TABLE 8. EFFECT OF AGING AN HCl- UROTROPIN SOLUTION (50 g/Liter Additive) FOR TIMES UP TO 24 HOURS PRIOR TO TESTING ON THE CORROSION CRACKING OF A 30 KhGSNA-TYPE STEEL WITH A STRENGTH OF 210 kg/mm<sup>2</sup> (299,000 psi)<sup>(23)</sup>

Composition of Solution	Time Solution Was Aged Before Testing, hours	Time to Cracking
5 percent HCl	--	15-20 seconds
5 percent HCl + urotropin	0	5-25 minutes
5 percent HCl + urotropin	2	48 minutes
5 percent HCl + urotropin	15	540 minutes
5 percent HCl + urotropin	24	>2 days
10 percent HCl + urotropin	24	>2 days
15 percent HCl	--	30 seconds
15 percent HCl + urotropin	0	15-40 minutes
15 percent HCl + urotropin	24	>2 days(a)

(a) Two samples out of ten cracked in 450 minutes.

These investigators pointed out that urotropin deserves special attention as an inhibitor, because, in contrast to the other inhibitors, it is readily soluble in water and leaves no stubborn film on the steel surface that would prevent the application of galvanic coatings. The investigators also pointed out an interesting finding - the inhibiting action of urotropin and of BA-6 depended greatly on the nature of the acid. This behavior probably results from a difference in surface charge; iron has a positive surface charge in sulfuric-acid solution and a negative charge in solutions containing chloride ion (Cl<sup>-</sup>). With a positive charge on the steel, the adsorption of polycations will be impeded and their inhibiting effect will be small. In hydrochloric acid, in which the steel surface is negatively charged, adsorption of the polycations is encouraged, so that their effect is much stronger in hydrochloric acid than in sulfuric acid. The investigators also concluded that there was no direct correlation between hydrogen absorption and cracking of the stressed high-strength steels during acid pickling. High-strength steels have a greater tendency toward corrosion cracking in hydrochloric acid than in sulfuric acid, although hydrogen absorption takes place more readily in sulfuric acid than in hydrochloric acid. For example, the transverse contraction (presumably reduction in cross section during a tensile test) of 30KhGSNA steel before pickling was 49 percent; after pickling for 30 minutes in a 20 percent sulfuric acid solution or in a 20 percent hydrochloric acid solution it was 14.8 percent and 33 percent, respectively. In addition, it is known that thiourea stimulates and diethylaniline retards hydrogen absorption of steel; however, the data from this investigation showed that thiourea reduced the tendency of the steel to crack by nearly the same amount as did diethylaniline.

Glasgow and associates investigated several acid-pickling formulations, with and without inhibitors, in an attempt to formulate a nonembrittling chemical-descaling treatment for very strong steels.<sup>(24)</sup> The steels used in this investigation were En40C and REX 539, both heat treated to the 115 to 120 tons/in.<sup>2</sup> (257 to 269 ksi) strength range. The criteria for the acceptability of the treatments were: (1) the treatment should not add more than 0.1 ppm hydrogen to the steel, (2) the treated steel should be a suitable substrate for a smooth, pore-free cadmium electroplate, and (3) the descaling mixture should remove the scale within a reasonable time, should not attack the underlying metal

too aggressively and should be reasonably stable. Hydrogen was extracted from heated samples in a low-pressure ( $10^{-3}$  mm Hg) enclosure, mixed with a standard volume of cylinder nitrogen at atmospheric pressure and temperature, and estimated with a katharometer previously calibrated with known hydrogen-nitrogen mixtures. Hydrogen was extracted in two stages in a closed static system; first at 250 C (482 F) for 1 hour and then at 650 C (1200 F) for 0.5 hour. Untreated samples were found to contain 0.01 to 0.02 ppm hydrogen extracted at 250 C plus 0.05-0.06 ppm extracted subsequently at 650 C. The following descaling treatments were evaluated in this investigation:

- (1) Reducing acids: hydrochloric, sulfuric, and orthophosphoric acids at concentrations of 20 percent by weight at 20 C (68 F) for 1 hour and 95 C (203 F) for 15 minutes
- (2) Pyrophosphoric acid: technical grade at temperatures from 100 to 200 C (212 to 392 F) and times from 3 to 4 hours at 100 C to 7 minutes at 200 C
- (3) Reducing acids plus proprietary restrainers
- (4) Proprietary alkaline derusters
- (5) Fused salts
- (6) Reducing acids plus oxidant mixtures
  - (a) Permanganate or ferric salt as oxidant: potassium permanganate plus sulfuric or phosphoric acid, ferric chloride plus hydrochloric acid, and ferric sulfate plus sulfuric or phosphoric acid at 20 C (68 F) for 1 hour or at 65 to 95 C (149 to 203 F) for 15 minutes; oxidant concentration 0.1M in 20 percent (by weight) acid solutions
  - (b) Nitric with sulfuric, phosphoric, or hydrofluoric acid: concentrated nitric acid (sp gr 1.42), in concentrations of 5 to 20 percent by volume in orthophosphoric acid or sulfuric acid (2 percent by volume). Aqueous solution of 5.3N hydrofluoric acid plus 1.6N nitric acid at 40 to 60 C (104 to 140 F) for 7 to 10 minutes
  - (c) Chromic-sulfuric and chromic-phosphoric acid mixtures
  - (d) Hydrogen peroxide-oxalic acid solutions.

The results of this investigation are presented in Tables 9 and 10. The dilute reducing-acid solutions, Table 9, were found to be unsatisfactory, because they introduced too much hydrogen into the steel. As shown in Table 10, all the acid mixtures that contained proprietary restrainers introduced too much hydrogen ( $>0.1$  ppm), and some did not descale effectively. The alkaline derusters that were studied introduced little additional hydrogen in the steel, but the rate of descaling in dilute solutions was very slow. More concentrated mixtures and mixtures containing added sodium hydroxide increased the descaling rate.

Addition of oxidants to the reducing mineral acids generally did not decrease hydrogen absorption. The nitric acid-containing chemical-polishing mixtures did provide a bright surface finish with fairly low hydrogen absorption (0.1-0.2 ppm); however, considerable attack of the base metal occurred during the first 1 to 5 minutes after immersion

TABLE 9. HYDROGEN CONTENTS OF PICKLED En 40C AND REX 539 STEELS AFTER PICKLING IN 20 WEIGHT PERCENT REDUCING-ACID SOLUTIONS(24)

Acid(a)	Temperature		Time, minutes	Hydrogen Extracted, ppm				Total Hydrogen Extracted, ppm	
	C	F		250 C		650 C		En 40C	REX 539
				En 40C	REX 539	En 40C	REX 539		
HCl	20	68	60	0.26	0.36	0.63	0.06	0.89	0.42
HCl	20	68	60	0.27	--	0.55	--	0.82	--
HCl	95	203	15	0.11	0.14	0.33	0.34	0.47	0.48
HCl	95	203	60	0.24	--	0.17	--	0.41	--
H <sub>2</sub> SO <sub>4</sub>	20	68	60	0.09	0.04	0.04	0.11	0.13	0.15
H <sub>2</sub> SO <sub>4</sub>	95	203	15	0.04	0.10	0.11	0.38	0.15	0.48
H <sub>3</sub> PO <sub>4</sub>	20	68	60	0.20	0.18	0.04	0.11	0.24	0.29
H <sub>3</sub> PO <sub>4</sub>	95	203	15	0.04	0.07	0.14	0.17	0.18	0.24
H <sub>3</sub> PO <sub>4</sub>	95	203	15	0.09	--	0.17	--	0.26	--

(a) Concentration = 20 percent by weight.

TABLE 10. EFFECT OF PICKLING FOR 30 MINUTES IN ACIDS CONTAINING PROPRIETARY RESTRAINERS ON THE HYDROGEN CONTENT OF En 40C STEEL

Restrainer <sup>(a)</sup>	Restrainer Concentration, volume percent	Acid	Acid Concentration, volume percent	Temperature, C	Hydrogen Extracted, ppm		Total Hydrogen Extracted, ppm	Weight Loss, mg/cm <sup>2</sup>
					250 C	650 C		
A	5	HCl	20	20	0.06	0.32	0.38	0.8
A	5	HCl	20	20	0.69	0.15	0.84	6.4
A	5	HCl	20	90	0.52	0.06	0.58	2.1
B	--	--	--	45	0.02	0.13	0.15	9.0
C	--	--	--	50	0.06	0.12	0.18	13
D	--	HCl	--	90	0.10	0.44	0.54	40
D	--	HCl	--	90	0.06	0.55	0.61	49
E	0.3	H <sub>3</sub> PO <sub>4</sub>	18	80	0.03	0.15	0.18	38
E	0.15	H <sub>3</sub> PO <sub>4</sub>	10	80	0.11	0.40	0.51	40

(a) A, an aliphatic nitrogenous inhibitor.

B, C, inhibited hydrochloric-phosphoric mixture, restrainer concentration not given.

D, inhibited hydrochloric acid, restrainer concentration not given.

E, dark-colored liquid containing heterocyclic compounds.



before polishing began. The chromic-sulfuric chemical-polishing mixtures attacked the metal to a lesser extent, with a fairly small increase in hydrogen content. The hydrogen peroxide-oxalic acid chemical-polishing mixtures show applicability, not for the removal of heavy scale but for improvement of the surface of steel previously descaled in a more aggressive medium.

Investigators at the Minnesota, Mining, and Manufacturing Company<sup>(25)</sup> have reportedly developed two classes of organic inhibitors that are effective in reducing hydrogen-stress-cracking failures in high-strength steels. Little information was available because of patent proceedings. However, their tests employing spring-wire hose clamps (Rockwell C hardness 54-58) showed that (after pickling 10 minutes in 2.5 to 10 percent sulfuric, hydrochloric, or phosphoric acid solutions at 75 F) out of 50 specimens stressed on a test block, only 1 or 2 had failed after 24 hours under stress. Specimens treated in a similar manner in uninhibited acids all failed the 24-hour test.

The mechanism by which inhibitors reduce attack on and limit hydrogen absorption by the base steel is still not definitely known, and many theories have been proposed. Among these are the overvoltage theory, the film theory, the electrolytic theory, the reducing theory, and the colloidal theory. (11, 12, 13, 14, 15, 16) It is likely that no single, generally satisfactory theory will cover the action of all inhibitor materials.

It is difficult to summarize the results of the numerous investigations of the effectiveness of pickling inhibitors for reducing hydrogen absorption by steels into a few general statements applicable to the objectives of the current research program. The difficulty arises from the fact that most of the work has been done on low-carbon, low-strength steels in which hydrogen-stress cracking is not a problem. In addition, compounds that effectively reduce corrosion do not necessarily reduce hydrogen absorption to the same extent, and in some instances they actually promote hydrogen absorption. Furthermore, the effectiveness of an inhibitor in an acid solution under a given set of conditions does not insure effectiveness in a different solution or even in the same solution under different conditions. Another problem is that quantitative data on commercial proprietary inhibitors reported to reduce hydrogen embrittlement generally are lacking. Nevertheless, several organic compounds have been shown to be quite effective in reducing attack on and hydrogen absorption by low-carbon steels during acid pickling. These compounds warrant further study to determine their effectiveness in reducing hydrogen embrittlement in the ultrahigh-strength steels of interest to the present program. These compounds are listed in the section on "Inhibitors and Cadmium-Electroplating Processes Recommended for Laboratory Evaluation".

#### LOW-HYDROGEN-EMBRITTLING CADMIUM-ELECTROPLATING PROCESSES

Cadmium electroplates on steel parts have been used extensively in the aircraft industry to provide galvanic protection against corrosion. However, cadmium electroplating from conventional cyanide baths has been shown to induce severe embrittlement in high-strength steels. As a result of the restrictions placed on cadmium electroplating of certain steels with strengths above 220 ksi, other methods of corrosion protection were used. But, most of these methods have been shown to provide less corrosion protection than does bright-cadmium electroplating. Consequently, considerable effort has

been expended in trying to develop cadmium-electroplating processes that are nonhydrogen embrittling and that produce deposits with corrosion-protection properties equal to those of bright-cadmium electroplates deposited from cyanide baths.

Several approaches have been tried in an attempt to develop nonembrittling electroplating procedures. Some of these are:

- (1) Deposition of porous plates at high current densities to facilitate subsequent removal of hydrogen by baking
- (2) Plating from 100 percent cathodically efficient electrolytes to prevent hydrogen codeposition
- (3) Barrier plating by depositing thin undercoats of cadmium or other metals, baking, and then overplating to the desired thickness
- (4) Suppression of hydrogen formation in aqueous electrolytes by suitable additions
- (5) Plating from organic baths that contain little or no ionizable hydrogen
- (6) Ultrasonic agitation during precleaning and electroplating.

The results of numerous investigations of these various approaches to the development of nonhydrogen-embrittling cadmium-electroplating procedures have been reviewed in the reports of the literature and industrial surveys conducted during the previous terms of this contract<sup>(1,2)</sup>. The following paragraphs review the significant results of these investigations with the limited amount of new information woven in at appropriate places.

Several investigations have shown that cadmium deposits from high-efficiency cyanide baths, baths without brighteners, and baths operated at high current densities are porous. Consequently, postplating baking at 375 F for 23 hours usually completely relieves any embrittlement. However, the appearance of these plates is not satisfactory, and their corrosion-protection properties are questionable. When brighteners are added to these baths to produce smooth, bright, fine-grained deposits, the specimens are embrittled and the usual baking treatment does not relieve the embrittlement, as is shown in Table 11. Therefore, even though porous cadmium plates can minimize hydrogen embrittlement, they are not completely desirable, and the search for more desirable systems has continued.

The hydrogen-embrittling tendencies of the cadmium-fluoborate electroplating process have been evaluated by many investigators and this bath has been shown to be less embrittling than are the conventional cyanide-cadmium processes. (27, 28, 29, 30, 31) The cadmium-fluoborate bath operates at nearly 100 percent plating efficiency, and, since hydrogen evolution is inversely related to efficiency, very little hydrogen is evolved. As a result, much less hydrogen is available to enter the steel during fluoborate-cadmium plating as compared with that available in conventional cyanide-cadmium plating. Although the fluoborate-cadmium process has been shown to be less embrittling than conventional cyanide-cadmium baths, it requires careful control and lacks the throwing power and covering properties of the cyanide bath.

TABLE 11. RESULTS OF SUSTAINED-LOAD EXPERIMENTS EMPLOYING NOTCHED TENSILE SPECIMENS  
CADMIUM PLATED IN HIGH-EFFICIENCY BATHS WITH AND WITHOUT BRIGHTENERS

Material	Ultimate Tensile- Strength Range, ksi	Tensile Strength of Unplated Notched Bar, psi	Plating Bath(a)	Current Density, asf	Baking Treatment	Applied Stress, percent NTS(b)	Time to Failure, hr	Failures/Number of Specimens	Reference
AMS 6427	220-240	330, $K_t = 3.2$	H. E. Bright Cad.	20	23 hr at 375 F	75	7	2 of 2	26
AISI 4340	260-280	360, $K_t = 3.2$	H. E. Bright Cad.	20	23 hr at 375 F	75	26	3 of 3	26
4340-1.5Si	270-300	376, $K_t = 3.2$	H. E. Bright Cad.	20	23 hr at 375 F	75	600	0 of 2	26
AMS 6427	220-240	330, $K_t = 3.2$	H. E. Cad.	20	23 hr at 375 F	75	150	0 of 2	26
AISI 4340	260-280	360, $K_t = 3.2$	H. E. Cad.	20	23 hr at 375 F	75	140	3 of 3	26
AISI 4340	260-280	360, $K_t = 3.2$	H. E. Cad.	40	23 hr at 375 F	75-90	200	0 of 16	26
AISI 4340	290	435, $K_t = 2$	H. E. Cad.	36	23 hr at 375 F	69	694	0 of 3	27
AISI 4340	290	435, $K_t = 2$	H. E. Bright Cad.	36	23 hr at 375 F	69	33	1 of 1	27

(a) H. E. Bright Cad. = High-efficiency cadmium both containing proprietary brightener.

H. E. Cad. = High-efficiency cadmium bath without brightener.

(b) NTS = notched-bar tensile strength.



Another method of minimizing embrittlement as a result of cadmium electroplating involves the use of a two-layer process<sup>(31, 32, 33, 34, 35)</sup>. This process consists of the deposition of a thin layer of cadmium or other metal such as copper or nickel, baking the specimen to relieve embrittlement, and overplating the thin, barrier deposit with cadmium until the desired plate thickness is obtained. Most of the investigations that have reported this technique to be successful in eliminating hydrogen embrittlement have used the criterion of restoration of original ductility as measured in a conventional tensile test to indicate freedom from embrittlement. Satisfying this criterion does not ensure freedom from hydrogen-stress cracking in a sustained-load test. Subsequent investigations of this approach employing sustained-load tensile tests have indicated a less beneficial effect from the use of undercoats in minimizing hydrogen embrittlement than was indicated by conventional tensile tests. For cadmium undercoats, it has been shown that thin, bright deposits have a greater tendency to minimize hydrogen embrittlement than do undercoats deposited from baths without brighteners. For metallic undercoats other than cadmium, it has been shown that the beneficial effects of these barrier plates generally increase with their thicknesses. However, this two-layer, barrier-plating approach has not received widespread use in attempts to minimize hydrogen embrittlement of high-strength steels, presumably because it has been shown that the method is not always effective and because it involves more processing steps than conventional plating.

Several organic cadmium-electroplating baths have been shown to be essentially nonhydrogen embrittling. Some of this work was performed by Vlannes and associates; part was described by them in Reference 36, and this and other work of theirs was described by Serota<sup>(37)</sup>. These investigators studied the plating characteristics and hydrogen-embrittling tendencies of several amino acid cadmium-plating solutions. Sustained-load tests were performed in which notched tensile specimens of AISI 4340 steel heat treated to the 285,000-psi tensile-strength level (smooth specimen) were loaded to an applied stress equivalent to 75 percent of the notched-bar tensile strength of the unplated bar. Cadmium was present in the form of cadmium sulfate, and cadmium anodes were used. The results of this study are shown in Table 12. All of the baths evaluated were found to be less embrittling than the standard cyanide bath.

The promising results obtained with the cadmium glycinate bath led to the development of the triethanolamine bath<sup>(38)</sup>. This organic base, in addition to controlling the pH of the bath, served also as a complexing agent (formed a complex ion with the metal salt).

A number of baths of two main types were studied: (1) a modified glycine bath [1 mole/l cadmium; 0.1-0.2 mole/l glycine; and 0.25-3.77 moles/l triethanolamine (TEAG)] and (2) glycine-free baths; (a) [1 mole/l cadmium, 0.25-3.75 moles/l triethanolamine (TEA)], (b) solutions containing 100-300, 500, and 600 grams of  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , and  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , respectively, in 1 liter of pure triethanolamine. Results of barrel plating from both types of baths showed that plating with a 24-hour cycle for 30 days without attention, other than maintaining constant volume with distilled water and periodic change of anodes, was feasible. Sustained-load tests with cylindrical, notched specimens of steel heat treated to 285,000-psi ultimate tensile strength and loaded to 75 percent of the tensile strength of a notched bar, showed that 40 out of 43 bars (93 percent), electroplated in the TEA bath with the current density carefully controlled, survived 100 hours. These results indicate that these baths are less embrittling than the conventional cyanide cadmium-plating bath.

TABLE 12. RESULTS OF SUSTAINED-LOAD EXPERIMENTS(a) TO DETERMINE THE HYDROGEN-EMBRITTLING TENDENCIES OF ALIPHATIC AMINO ACID CADMIUM-ELECTROPLATING BATHS(36, 37)

Bath	Cd Content, moles/l	Amino-Acid Content, moles/l	pH	Bars Broken in Less Than 100 Hours			Bars Unbroken After 100 Hours	
				Average Survival Time, hours	Number of Bars	Percent of Total Number	Number of Bars	Percent of Total Number
Glycinate	1	2	9.73	5	10	34	19	66
$\beta$ -Alaninate	2	2	9.20	--	--	--	2	100
	1	2	9.81	6	3	50	3	50
$\alpha$ -Amino-n-butyrate	2	2	10.62	--	--	--	3	100
	1	2	9.52	4	18	47	20	53
$\alpha$ -Amino-isobutyrate	2	2	9.32	--	--	--	3	100
	1	2	9.60	6	18	42	11	58
$\alpha$ -Amino-n-caproate	2	2	9.35	--	--	--	2	100
	1	0.191	11.12	10	1	33	2	67
$\alpha$ -Amino-isocaproate	2	0.191	11.05	--	--	--	3	100
	1	0.152	10.87	2	1	20	4	80
Cyanide Bath(b)	2	0.152	10.89	--	--	--	1	100
	--	--	--	0.02	9	100	--	--

(a) Specimens were AISI 4340 steel, heat treated to 285,000 psi ultimate tensile strength; notch root radius 0.001 inch; stressed at 75 percent of the notched-bar tensile strength.

(b) Cyanide bath 3.5 oz/gal CdO and 17 oz/gal NaCN plus 12 oz of brightener per 100 gal.

A nonaqueous cadmium-plating bath, with methanol as a solvent, was investigated with solutions containing 0.9-1.35 moles/l of cadmium acetate,  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ <sup>(37)</sup>. This plating bath gave satisfactory results in the Hull-cell test and showed a high water tolerance. The addition of triethanolamine to a cadmium-methanol solution also resulted in satisfactory deposits as determined by the Hull-cell tests. Embrittlement characteristics were determined by means of sustained-load tests and the results indicated non-embrittlement: 20 of 20 specimens electroplated from the methanol solution survived the 100-hour test, and 27 out of 27 specimens plated from the methanol-triethanolamine bath showed the same results. Continuous tank plating from the baths was found possible for 24 hours a day for 30 days, without attention other than volume control and anode renewal.

Pyridine,  $\text{C}_5\text{H}_5\text{N}$ , a cyclic tertiary amine, is another complexing agent that was studied as a potential aqueous nonembrittling cadmium-electroplating solution<sup>(37)</sup>. Room temperature was found to be most favorable for plating steel using cadmium concentrations not greater than 1 mole/l. At a pyridine content of 30 percent by volume and current densities of 12.8 to 15 asf, a semibright deposit was obtained. Two inorganic additions, 0.1 gram per liter of chromic acetate or nickelous chloride, and two organic additives, 10 ml per liter of 2-naphthalene sulfonic acid or p-toluene sulfonic acid, were found to improve the appearance of the deposit. Sustained-load tests reportedly showed nonembrittling characteristics, but no data were given.

Another organic cadmium-plating bath that has been reported to be nonhydrogen embrittling is the dimethylformamide (DMF) bath developed by Grumman Aircraft.<sup>(39)</sup> The cadmium is supplied by cadmium iodide and cadmium anodes.

The results of investigations employing notched tensile specimens of AISI 4340 steel (260 to 280-ksi strength) that were electroplated by the DMF process are contradictory. In one study, DMF-plated notched tensile specimens failed in the sustained-load test at applied stresses of 180,000 psi.<sup>(40)</sup> In another study, 18 notched tensile specimens survived applied stresses equal to 75 percent of the notched-bar tensile strength of unplated specimens and 5 specimens survived applied stresses of 90 percent of the notched-bar tensile strength.<sup>(39)</sup> In both of these studies, the specimens were prepared for electroplating by mechanical cleaning, and no postplating baking treatment was employed. It was reported, also, that the adhesion and corrosion protection obtained with the cadmium deposit from the DMF bath compared favorably with those of deposits obtained from the aqueous cyanide plating bath.

In the evaluation of the hydrogen-embrittling tendencies of the DMF cadmium-electroplating bath conducted during a previous term of this contract, notched-tensile specimens of AISI 4340 steel (260-ksi ultimate tensile strength) failed after 198 and 254 hours at applied stresses equal to 90 percent of the tensile strength of an unplated notched bar.<sup>(41)</sup> Notched tensile specimens of AISI Type H-11 tool steel and 18Ni(250) maraging steel, both heat treated to the 260-ksi ultimate-tensile-strength level, survived over 390 hours at applied stresses equal to 90 percent of their respective notched-bar tensile strengths.

One reportedly low-hydrogen-embrittling process that has received considerable study is the cadmium-titanium (Delta) process that was developed by the Japanese. The plating solution is similar to that of a conventional cyanide cadmium-electroplating solution, except that titanium is held in suspension in the plating system.<sup>(42,43)</sup> For low-embrittlement cadmium-titanium plating, nonembrittling-cleaning and activation processes are used, and the bath is operated without brighteners to produce a deposit with

controlled porosity. While this approach is essentially the same as that of conventional low-embrittling baths, the addition of titanium results in several significant improvements. One of these is that adequate hydrogen-embrittlement relief can be obtained with less plate porosity than with other low-embrittlement processes because the steel picks up less hydrogen during cadmium-titanium electroplating. (42, 43, 44) In addition, the baking times required to provide adequate embrittlement relief are generally shorter, and, contrary to the behavior of conventional cadmium electroplates, the degree of embrittlement relief has been reported to increase with increasing thickness of the cadmium-titanium electroplate (45). Another significant advantage of the cadmium-titanium electrodeposit is its superior corrosion resistance. In various salt-spray tests, cadmium-titanium deposits have been shown to be several times as corrosion resistant as conventional cadmium electroplates (42, 46). The inherent lack of precision of corrosion tests makes it virtually impossible to develop quantitative data on the corrosion resistance of electroplates; however, some investigators have reported no basis-metal corrosion on cadmium-titanium plated panels after more than 2000 hours of salt-spray exposure. In comparison, conventional cadmium electroplates have failed within 200 to 500 hours. (42)

Tables 13 and 14 present the results of several evaluations of the hydrogen-embrittling tendencies of the cadmium-titanium electroplating process and the corrosion resistance of the resulting electroplates, respectively.

Several companies use the cadmium-titanium process for electroplating aircraft components. Menasco Manufacturing Company has used this process to electroplate landing gear and other heavy structural components for a commercial jet airline. Boeing has used the cadmium-titanium (Delta) process to electroplate landing struts, flap carriages, and flap tracks for the Boeing 727 jet airliner.

A selective-plating process that has been reported to be nonhydrogen embrittling was developed by Selectrons, Ltd. (49) The Selectron Cadmium LHE process has been reported to permit rapid deposition of cadmium on ultrahigh-strength steels without introducing significant hydrogen embrittlement. These deposits have fulfilled the requirements of specification QQ-P-416a without being baked after plating. (50) It also has been reported that the corrosion resistance of this cadmium electroplate is equivalent to that of conventional cadmium electroplates if the manufacturer's recommended practices are followed. At least 13 companies reportedly have authorized the use of the Selectrons LHE cadmium-electroplating process on steels with tensile strengths in excess of 240,000 psi, and the process has received fairly widespread use by aircraft maintenance depots for repair plating of aircraft parts. (51) Some work has been done to evaluate this plating solution in bath form. Although quantitative data from sustained-load tests are lacking, results obtained with a Lawrence hydrogen gage indicated that hydrogen penetration with the cadmium LHE process was approximately 10 percent of that obtained when using the cadmium-titanium (Delta) process, which has been shown to introduce less hydrogen than a conventional cyanide bath. Other tests are in progress to determine the hydrogen-embrittling tendencies of the Selectron LHE cadmium solution as a bath.

Table 15 presents some of the results of an evaluation of the cadmium LHE process reported by Jankowsky. (50) These data show that this process was nonembrittling under the test conditions used.

Dingley and associates have reported a cadmium-electroplating process for use on high-strength steels without development of significant hydrogen embrittlement. (8, 9) The bath used in this process is a stabilized cadmium cyanide bath. The most important



TABLE 13. RESULTS OF SUSTAINED-LOAD EXPERIMENTS EMPLOYING NOTCHED TENSILE SPECIMENS OF SEVERAL ULTRAHIGH-STRENGTH STEELS ELECTROPLATED IN THE CADMIUM-TITANIUM (DELTA) BATH

Base Steel	Ultimate Tensile Strength, ksi	Notched-Bar Tensile Strength, ksi	Post-Plate-Baking Treatment	Applied Stress, percent NTS(a)	Duration of Test, hr	Failure	Reference
AISI Type H-11	(b)	330	None	75	1,300	No	47
AISI Type H-11	(b)	330	None	75	1,994	No	47
AISI 4340 Steel	260-280	340	(b)	75	200	No	43
4330 M(c)	220-240	334	(b)	75	700	No	43
98BV40	275	338	None	75	0.8	Yes	45
98BV40	275	338	None	75	3.4	Yes	45
98BV40	275	338	24 hr, 375 F	75	58.3	Yes	45
98BV40	275	338	24 hr, 375 F	75	84.7	Yes	45
98BV40	275	338	24 hr, 375 F	75	101.8	No	45
				90	8.4	Yes	45
AISI 4340 Steel	260	314	None	75	143	No	52
				90	8.8	Yes	52
AISI 4340 Steel	260	314	None	75	125.6	Yes	52
AISI 4340 Steel	260	314	12 hr, 390 F	75	143	No	52
				90	81.1	Yes	52
AISI 4340 Steel	260	314	12 hr, 390 F	75	144	No	52
				90	31.4	Yes	52
AISI Type H-11	260	338	None	75	143	No	52
AISI Type H-11	260	338	12 hr, 390 F	75	217	No	52
				90	143	No	52
18Ni (250)	260	407	None	75	217	No	52
Maraging Steel				90	143	No	52
18Ni (250)	260	407	12 hr, 390 F	75	217	No	52
Maraging Steel				90	144	No	52
				90	190	No	52

(a) NTS = notched bar tensile strength.

(b) Information not provided.

(c) AMS 6427.

TABLE 14. RESULTS OF CORROSION TESTS PERFORMED ON CADMIUM-TITANIUM (DELTA)-PLATED AND CONVENTIONAL CADMIUM-PLATED STEEL PANELS

Base Steel	Electroplate	Plate		Test		Remarks	Reference
		Thickness, mil	Exposure Conditions	Duration, hr			
--	Cd-Ti, bright chromate	0.5	ASTM-B-117(a)	2,000	No red rust	46	
--	Cd-Ti, bright chromate	0.3	ASTM-B-117(a)	2,000	No red rust	46	
--	Cd-Ti, bright chromate	0.5	ASTM-B-368-61T(b)	24	No red rust	46	
--	Cd-Ti, bright chromate	0.3	ASTM-B-368-61T(b)	24	No red rust	46	
--	Cd-Ti, 68 ppm Ti	0.4	Salt spray	500	No rust	48	
--	Cd-Ti, 68 ppm Ti	0.5	Salt spray	500	No rust	48	
--	Cd-Ti, 84 ppm Ti	0.5	Salt spray	500	No rust	48	
--	Cd-Ti, 84 ppm Ti	0.5	Salt spray	500	No rust	48	
--	Cd-Ti, 139 ppm Ti	0.3	Salt spray	500	No rust	48	
--	Cd-Ti, 139 ppm Ti	0.4	Salt spray	500	No rust	48	
AISI 4130	Cd-Ti	0.45	ASTM B-117-57T(a)	1,390	No rust	47	
AISI 4130	Cd-Ti	0.45	ASTM B-117-57T(a)	1,390	No rust	47	
AISI 4130	Cd	0.45	ASTM B-117-57T(a)	1,390	No rust, more pitting	47	
AISI 4130	Cd	0.45	ASTM B-117-57T(a)	1,390	No rust, more pitting	47	

(a) ASTM B-117 and ASTM B-117-57T, 5 percent neutral salt spray.

(b) ASTM B-368-61T, Cass test, copper-accelerated acetic acid salt spray.

TABLE 15. RESULTS OF TESTS WITH NOTCHED C-RING SPECIMENS TO EVALUATE THE HYDROGEN-EMBRITTLMENT TENDENCIES OF VARIOUS SELECTRON CADMIUM-PLATING PROCESSES<sup>(50)</sup>

Material: AISI 4340 steel; 260 to 280-ksi strength level

Process	Applied Stress, percent NTS <sup>(a)</sup>	Time for Failure
<u>A. Results With Rings Stressed After Plating</u>		
Standard Selectron	82	5 min
Standard Selectron	82	1 min
Standard Selectron	75	15 min
Standard Selectron	75	1 hr and 15 min
Selectron Type FC	82	5 hr and 26 min
Selectron Type FC	82	1 hr
Selectron Type FC	75	3 hrs and 32 min
Selectron Type FC	75	31 hr
Selectron Type LHE	82	40 hr <sup>(b)</sup>
Selectron Type LHE	82	40 hr <sup>(b)</sup>
Selectron Type LHE	75	200 hr <sup>(b)</sup>
Selectron Type LHE	75	200 hr <sup>(b)</sup>
Conventional Cyanide Cd	82	Failed on loading
Conventional Cyanide Cd	82	Failed on loading
<u>B. Results With Prestressed Rings</u>		
Standard Selectron	50	Failed during plating
Standard Selectron	50	Failed during plating
Selectron Type FC	50	Failed during plating
Selectron Type FC	50	Failed during plating
Selectron Type LHE	50	72 hr <sup>(b)</sup>
Selectron Type LHE	50	72 hr <sup>(b)</sup>
Conventional Cyanide Cd	50	Failed during plating
Conventional Cyanide Cd	50	Failed during plating

(a) NTS = notched-bar tensile strength.

(b) Specimen did not fail in time indicated.

conditions for stability of the cadmium bath are (1) OH normality = CN normality and (2) CN normality/cadmium normality = 3.6 to 3.8. In addition to the development of the low-embrittling cadmium-plating bath, the investigators developed a preplating cleaning process that does not induce significant embrittlement.

The majority of the work with these cleaning and electroplating processes was done using pins of AISI 1062 steel (Rockwell C hardness 52-56) and AISI 4037 steel (Rockwell C hardness 51-55). The method of detecting embrittlement was the constant-rate bend test (a method that is not as sensitive in detecting embrittlement as the sustained-load test). The results of the experiments to evaluate the hydrogen-embrittling tendencies of various preplating cleaning treatments are presented in Table 16.

The AISI 1062 and AISI 4037 steel pins were free from significant hydrogen embrittlement after processing by a procedure that included dipping in hydrochloric acid, dipping in a copper sulfate solution, treatment in a solution of nitric and acetic acids, and rinsing under the influence of ultrasonics. It was reported that a procedure involving the use of nitric acid instead of a combination of nitric and acetic acids, and eliminating the use of the copper sulfate solution, also gave freedom from significant embrittlement. However, this treatment gave a rougher surface and an excessive loss of metal because of the much more rapid reaction rate.

Nonembrittling pretreatment and subsequent plating in a stabilized cadmium bath resulted in pins that contained no hydrogen embrittlement detectable in the bend test. These results are shown in Table 17.

The investigators have conducted a few sustained-load tests to evaluate the embrittling tendencies of the cleaning and cadmium-electroplating procedures developed. In these experiments, notched tensile specimens of AISI 4340 steel heat treated to the 250 to 280-ksi ultimate-tensile-strength range were used; the applied stress levels were not given. Of eight specimens evaluated, six have failed in times ranging from 140 to 480 hours and two have remained unbroken after 504 hours of test. None of these bars were baked after plating. For comparison, similar specimens plated with cadmium by typical commercial procedures failed during loading.

The electroplating processes described in this report are reported to be essentially nonhydrogen embrittling under the conditions evaluated. However, until the basic mechanism of hydrogen embrittlement of steels is completely understood and more quantitative data with respect to hydrogen in steel become available, it is meaningless to merely state that a process is embrittling or nonembrittling. Variables that must be considered are the composition of the steel used to evaluate the process, the strength level of the steel, the stress level used to determine the degree of embrittlement, the test method, and the ability of the coating to allow embrittlement relief. If these variables are fixed, then it could be stated that a process is embrittling or nonembrittling, but only for the fixed conditions.

In addition to considering the plating process itself, the entire processing history of the material used to evaluate the process must be considered. Sufficient hydrogen may be picked up during heat treating and preplating cleaning and activating processes to render the material susceptible to hydrogen-stress cracking regardless of the embrittling tendencies of the electroplating process. Therefore, all these preplating treatments must be evaluated and their ability to introduce embrittlement recognized. Those



TABLE 16. EMBRITTLEMENT OF AISI 1062 AND AISI 4037 STEEL PINS DURING VARIOUS SURFACE TREATMENTS<sup>(8)</sup>

Surface Treatment	Steel Type	Degree of Embrittlement	
		Angle of Bend at Fracture, degrees	Proportion of Pins Fractured, <sup>(a)</sup> percent
H <sub>2</sub> SO <sub>4</sub> (3 min), rinsed	1062	8-35	100
	4037	50-84	92
H <sub>2</sub> SO <sub>4</sub> (3 min) accompanied by ultrasonic vibration, rinsed	1062	45-78	100
	4037	58-119	75
HCl (3 min) rinsed	1062	65-120	50
	4037	30-129	87
Cathodic treatment in HCl	1062	< 10	100
	4037	< 10	100
HCl (3 min) accompanied by ultrasonic vibration, rinsed	1062	>135	0
	4037	68-99	60
HCl (1 min) with ultrasonics, rinsed	1062	>135	0
	4037	68-100	50
HCl (1 min) with ultrasonics, rinsed, HNO <sub>3</sub> (5 min), rinsed, rinsed with ultrasonics	1062	>135	0
	4037	>135	0
HCl (10 sec), rinsed, copper coat, rinsed HNO <sub>3</sub> -CH <sub>3</sub> COOH (1 to 5 min), rinsed, rinsed with ultrasonics	1062	>135	0
	4037	>135	0

(a) At bend angles of less than 135 degrees.

TABLE 17. EFFECT OF PRETREATING FOLLOWED BY PLATING IN A STABLE BATH, ON THE EMBRITTLEMENT OF AISI 1062 AND AISI 4037 STEEL PINS<sup>(8)</sup>

Procedure	Steel Type	Degree of Embrittlement After Plating	
		Angle of Bend at Fracture, degrees	Proportion of Pins Fractured, <sup>(b)</sup> percent
HCl (1 min) with ultrasonics, rinse, plate	1062	65-122	77
	4037	(a)	--
HCl (1 min) with ultrasonics, rinse, copper coat, rinse, HNO <sub>3</sub> -CH <sub>3</sub> COOH (A <sup>(c)</sup> ) 1 min, rinse, ultrasonic water rinse, HCl (1 min) with ultrasonics, rinse, plate	1062	>135	0
	4037	>135	0
HCl (10 sec), rinse, copper coat, rinse, HNO <sub>3</sub> -CH <sub>3</sub> COOH (B <sup>(d)</sup> ) 5 min, rinse, ultrasonic water rinse, plate	1062	>135	0
	4037	>135	0

(a) Not sufficiently clean for plating.

(b) At bend angles of less than 135 degrees.

(c) A - 15 percent by weight HNO<sub>3</sub>, 4 percent by weight CH<sub>3</sub>COOH.(d) B - 12 percent by weight HNO<sub>3</sub>, 34 percent by weight CH<sub>3</sub>COOH.

processes that introduce hydrogen should be eliminated or placed under strict control to eliminate hydrogen pickup.

### INHIBITORS AND CADMIUM ELECTROPLATING PROCESSES RECOMMENDED FOR LABORATORY EVALUATION

Although data on the effectiveness of inhibitors for reducing hydrogen absorption by high-strength steels are lacking, a number of organic compounds were reported to reduce hydrogen absorption by mild steels during acid pickling. Based on the data reviewed in the previous sections of this report it is recommended that the following compounds be considered for evaluation in the laboratory:

- (1) 1 Pentyn-3-ol, Table 2
- (2) 1 Hexyn-3-ol and 1-Hexyn-3-ol plus salt, Tables 2 and 5
- (3) 1-Ethynylcyclohexan-1-ol, Table 2
- (4) 4-Methyl-1-pentyn-3-ol, Table 2
- (5) n-Dodecylamine, Table 3
- (6) Ethomeen C/12 and ethomeen C/12 plus salt, Tables 3 and 5
- (7) Indole and indole plus salt, Tables 3, 5, and 6
- (8) Quinolene plus potassium iodide, Table 7
- (9) Quinolene ethiodide, Table 3
- (10) Hexamethylenetetramine, and hexamethylenetetramine plus salt, Tables 3, 5, and 7
- (11) Pyrrole plus salt, Table 5
- (12) 1-Methylpyrrole plus salt
- (13) Proprietary inhibitors from 3M Company.

Since no quantitative data were available for other proprietary materials, it is recommended that these materials be selected on the basis of information contained in the trade literature and evaluated according to the manufacturers' recommendations.

The cadmium-electroplating processes recommended for evaluation include the Selectron LHE process, the stable cadmium bath developed by Bednar and Dingley, and the methanol bath developed by Vlannes and associates, and described by Serota.

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