NAS8-20029

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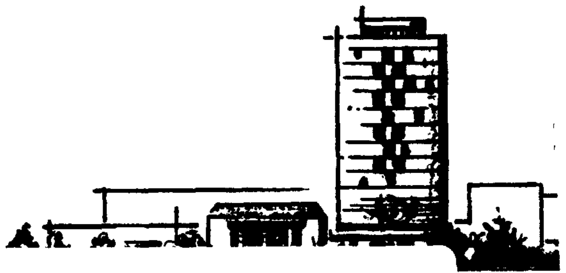

N67 13569	
(ACCESSION NUMBER)	(THRU)
44	1
(PAGES)	(CODE)
CR 80690	15
(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

FACILITY FORM 602

GPO PRICE $ ______

CFSTI PRICE(S) $ ______

Hard copy (HC) 2.00

Microfiche (MF) .50

ff 653 July 65

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SPECIAL REPORT

on

A REVIEW OF THE LITERATURE ON CLEANING, PICKLING, AND ELECTROPLATING PROCESSES AND RELIEF TREATMENTS TO MINIMIZE HYDROGEN EMBRITTLEMENT OF ULTRAHIGH-STRENGTH STEELS

to

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

October 15, 1966

by

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Ferrous and High Alloy Metallury Division
Process and Physical Metallurgy Department

Contract Number NAS 8-20029, Supplement 1
Control Number DCN 1-5-54-01112-01 (IF) & SI(IF)

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Columbus, Ohio 43201

This report was prepared by Battelle Memorial Institute under Contract Number NAS 8-20029, Supplement 1, "Study of Hydrogen Embrittlement of Various Alloys", for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. This work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Materials Division of the George C. Marshall Space Flight Center, with James R. Lowery acting as project manager.

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A REVIEW OF THE LITERATURE ON CLEANING, PICKLING, AND ELECTROPLATING PROCESSES AND RELIEF TREATMENTS TO MINIMIZE HYDROGEN EMBRITTLEMENT OF ULTRAHIGH-STRENGTH STEELS

by

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INTRODUCTION

Atomic hydrogen is capable of entering steel and many other metals and alloys; when it does, any of several undesirable phenomena can occur. If large quantities of hydrogen are introduced, there may be a general loss in ductility or, if the hydrogen accumulates in certain localized areas, internal bursts or blisters may be produced. At elevated temperatures, hydrogen may react with and remove so much carbon from the steel that the material is no longer capable of supporting the design stresses. Under certain circumstances, hydrogen introduced into steel during its manufacture, subsequent fabrication, or in service may result in brittle failures at applied stresses far below the yield strength or the nominal design stress for the alloy. All of these phenomena are collectively referred to as hydrogen embrittlement. However, only the last i.e., the catastrophic, hydrogen-induced, brittle failure of ultrahigh-strength structural steels at relatively low applied stresses is of interest in the present program. Since this phenomenon frequently occurs in materials that exhibit no appreciable loss in ductility (as measured by a conventional tensile test), it is often termed hydrogen-induced, delayed brittle failure, or hydrogen-stress cracking.

It has been shown that several conditions must be satisfied for hydrogen-stress cracking of steels to occur:

(1) The steel must be processed to a strength level above some as yet not clearly defined minimum*; generally, as the strength level of the steel is increased above this minimum, the time for failure decreases.

(2) The steel must be subjected to an applied tensile stress above some minimum value that is dependent on the strength level of the steel; as the strength level of the steel increases, the minimum applied stress that will result in hydrogen-stress cracking decreases.

(3) The steel must contain hydrogen in excess of some minimum amount, and this hydrogen must be free to diffuse through the steel.

In view of these conditions, it would be expected that any condition that alters the strength, applied stress, or hydrogen content of a given material could influence its sensitivity to hydrogen-stress cracking. The trend toward higher tensile strengths, higher design stresses, and the use of materials in applications requiring prolonged exposure to high sustained loads insures that two of the conditions necessary for the

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*No well-authenticated failures have resulted from hydrogen-stress cracking in steels with ultimate tensile strengths below 100,000 psi.

occurrence of hydrogen-stress cracking will be present in steel parts intended for certain aerospace and aircraft applications. All that remains is for an adequate supply of hydrogen to be available and for this hydrogen to be free to diffuse through the steel. Thus, it appears that, for high-strength steels sensitive to hydrogen-stress cracking, the most important factors tending to promote hydrogen-stress cracking under these conditions are the hydrogen content of the material and the propensity of the material to absorb hydrogen from its environment, either during processing or in service.

The source of the hydrogen in the metal is of little importance. It can be introduced during steelmaking or heat-treating operations; during cleaning, pickling, or electroplating processes; or it may be picked up from the service environment as a result of cathodic protection reactions or corrosion reactions, for example. In short, any process that presents atomic hydrogen to the steel, whether by thermally activated dissociation of hydrogen-gas molecules, electrochemical reaction, or chemical reaction, is capable of introducing sufficient hydrogen to cause failure. Unless such processes are avoided, or unless the hydrogen introduced is removed from ultrahigh-strength steels before permanent damage occurs, the potential exists for failure of these materials in service.

The problem of hydrogen-stress cracking of ultrahigh-strength steels has become quite serious in the aerospace and aircraft industries because many of the components fabricated from 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 can make the part susceptible to failure by hydrogen-stress cracking because, frequently, hydrogen is introduced during the cleaning and electroplating operation.

As a result of failures attributed to hydrogen-stress cracking and because of the possibility that additional failures might occur, the Air Force a few years ago prohibited the use of cadmium electroplating of certain steels having 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 cadmium electroplating. 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 enbrittled to various degrees by virtually all of the common electroplating processes, including cadmium, chromium, zinc, tin, nickel, lead, copper, and silver. These early 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. 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.

A report was prepared during the previous contract period, that described the results of a literature and industrial survey on hydrogen embrittlement resulting from conventional cleaning, pickling, and electroplating processes(1)*; the results of numerous investigations into this problem area were included. Several cleaning and

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*References are listed at the end of this report, beginning on page 37.

electroplating processes that were reported to be essentially nonhydrogen embrittling also were described. In addition, a review of the hydrogen embrittlement of steels, nickel-base alloys, and titanium alloys was presented. This report served as the background for the present survey.

The present report describes the results of a literature and industrial survey of reportedly low-hydrogen-embrittling and nonhydrogen-embrittling cleaning, pickling, and electroplating processes (including cadmium, chromium, and nickel electroplating) and of various hydrogen-embrittlement relief treatments. No attempt has been made to repeat the information on the embrittling effects of conventional processes in the present report. However, it was found desirable to include some reference to work described previously (especially in the area of cleaning processes) to provide necessary background information or to make desirable comparisons.

The main purpose in conducting the present survey was to obtain information to aid in the selection of cleaning and electroplating processes to be studied in the present term of the research program.

NONHYDROGEN-EMBRITTLING CLEANING AND PICKLING PROCESSES

During processing and fabrication, metals and alloys frequently acquire scale or oxide coatings, as well as other surface contamination, such as oil, grease, and dirt. It is essential that parts be clean before painting or electroplating them, if satisfactory adherence is to be obtained. Therefore, various cleaning processes are employed to remove the surface contaminants. The cleaning processes commonly employed for the removal of surface oxides include mechanical cleaning (such as grit blasting and tumbling), salt-bath descaling, alkaline descaling, and acid pickling; those commonly used for the removal of oil, grease, and dirt are alkaline cleaning, emulsion cleaning, solvent cleaning, and vapor degreasing(2). Some of these cleaning processes may be performed cathodically or anodically to facilitate the cleaning action.

Selection of the cleaning process is influenced mainly by the type of surface contamination to be removed, the required degree of cleanliness, and the cost.

Those processes commonly employed in the cleaning of steels that are considered to be nonhydrogen-embrittling processes include dry mechanical cleaning, solvent cleaning, vapor degreasing, and anodic cleaning (acid or alkaline). Although there are few data in the literature on the embrittling tendencies of these cleaning processes, none of the processes depend for their cleaning action on a reaction that deposits atomic hydrogen on the workpiece.

In many studies in which the embrittling tendencies of various electroplating processes have been evaluated, investigators have prepared the specimens by vapor degreasing and dry-abrasive cleaning. In no case was it reported that the test specimens were embrittled after this preparation. However, Swets, Frank, and Fry(3) using a sensitive ion-gage detector, demonstrated that hydrogen permeated an SAE 4340 steel cylinder with a wall thickness of 0.020 inch during abrasion with dry abrasive paper. When the abrasive paper was soaked in water, the permeation rate increased significantly. This behavior was attributed to simple corrosion that was accelerated by continual exposure of fresh metal during abrasion. Water vapor in the air constituted the source of hydrogen when dry abrasive paper was used.

Anodic cleaning processes are nonhydrogen embrittling, because the workpiece is made the anode during electrolysis and, consequently, no hydrogen is deposited on it. However, when anodic cleaning processes – particularly acid anodic cleaning processes – are used, the parts should be placed in the bath with the current on to prevent hydrogen pickup due to chemical reaction with the electrolyte. Also, the parts must be rinsed thoroughly immediately after completion of the anodic treatment to minimize any pickling or corrosion reactions that might occur as a result of cleaning solution remaining on the parts. Also, rinse baths should be changed continually to prevent undue contamination by the cleaning solutions; this is especially important if the cleaning solutions are acidic. In this respect, investigators at Boeing(4), using the Lawrence hydrogen-detection gage, found that the rinses following pickling and electroplating introduced considerable hydrogen into the parts being treated. They changed their process by requiring that the parts be rinsed in overflow tanks in which the rinse baths are changed at least once every hour.

Probert and Rollinson(5) found that anodic treatment of several high-strength steels in dilute sulfuric acid at room temperature for 1 minute induced some embrittlement. However, when they employed the procedures described previously to minimize pickling reactions before and after the actual anodic treatment, embrittlement was negligible except on high-carbon steels, which apparently are embrittled by very small amounts of hydrogen. These investigators also found that by anodically removing about 3 mils of material from steels that were severely embrittled by cathodic cleaning processes, full ductility (as measured by a slow-bend test) was restored(6). However, as pointed out in the introduction, restoration of ductility does not necessarily indicate freedom from hydrogen-stress cracking as measured by the more sensitive sustained-load test.

Alkaline descaling also has been reported to provide complete freedom from hydrogen embrittlement(2). This process also has the advantage of not attacking the base metal; this is because the chemical reaction stops when rust or scale removal is complete. However, alkaline descaling is more costly and slower in its action than acid pickling. A number of proprietary alkaline descaling compounds are available; they are composed primarily of sodium hydroxide (60 percent or more), but also contain chelating agents.

In spite of its embrittling effects on ultrahigh-strength steels, acid pickling is still the most commonly used descaling method, because it is generally cheaper, it usually does not require special equipment or controls, and, except for mechanical descaling, it is generally faster than other methods. Consequently, the greater portion of the effort expended in evaluating hydrogen embrittlement that results from cleaning processes and in developing low-embrittling procedures has been expended on acid-pickling processes.

It has been shown that nearly all common acid-pickling processes can severely embrittle ultrahigh-strength steels and that cathodic pickling increases the embrittlement(1). However, oxidizing acids (particularly nitric acid) have been reported to be essentially nonhydrogen embrittling(7,8). The unique behavior of nitric acid with respect to hydrogen embrittlement is related to its oxidizing characteristics. Metals react with nitric acid by replacing hydrogen to form the corresponding nitrates, and the hydrogen evolved during this process is immediately consumed, with the formation of compounds containing nitrogen of lower valency. However, Balezin and Nikol'skii(9, 10) and Hudson, Norris, and Stragand(11) reported that under certain circumstances nitric acid solutions can cause embrittlement of steel. Balezin and Nikol'skii found that steels containing 0.17, 0.6, 0.9, and 1.1 percent carbon, respectively, did not absorb hydrogen when pickled in 1.5 N and 2N nitric acid solutions, but did absorb hydrogen in 0.5 N nitric acid solution. The range of nitric acid concentration that produced the most severe embrittlement in steel wire at 64 F was from 0.3 to 0.8 N. They attributed this embrittlement to the likelihood that not all of the hydrogen evolved was oxidized.

The reason why oxidizing acids are not employed more widely as a simple means of avoiding hydrogen troubles without resorting to an external potential is that practically every oxidizing acid or acidic mixture introduces some new objection. Nitric acid, for example, is unpleasant because of the fumes evolved and because of its action on the skin.

The method most frequently used to reduce problems related to both metal attack and hydrogen liberation in acid pickling is to add inhibitors to the pickling bath. Until the hydrogen embrittlement of ultrahigh-strength steels became a serious problem, inhibitors were used primarily to minimize metal loss, to protect the metal against pitting (caused by overpickling) and reduction in surface quality, to reduce acid fumes resulting from excessive reaction between the acid and basis metal, and to reduce acid consumption. Even at the present time, for lower strength steels these functions are still the primary reasons for adding inhibitors to acid pickling baths.

With the trend toward the use of steels for structural applications at increasingly higher strength levels, hydrogen-stress cracking became a problem to be reckoned with in the 1950s. Since that time, many evaluations of the effectiveness of inhibitors for reducing hydrogen pickup from pickling baths have been conducted.

Evans(12), in describing the use of inhibitors to minimize hydrogen embrittlement, pointed out that if the only objective in using an inhibitor is to reduce the metal loss and the consumption of acid, any substance that obstructs any one of the several essential steps of the corrosion process, such as the anodic reaction or the cathodic reaction, can be used. However, in practice, an inhibitor must meet other requirements. Reducing the total metal corrosion, which is equivalent to reducing the total amount of hydrogen produced, does not suffice. It is particularly necessary to reduce that fraction of the hydrogen that enters the metal and causes either blistering or cracking.

Zapffe and Haslem(13) studied the effects of 15 commercial inhibitors on hydrogen embrittlement and found that the chemical composition of the steel was the deciding factor in determining the efficiency of the inhibitor. Practically all the commercial inhibitors failed completely when pickling stainless steel. In fact, 11 of them were reported to increase hydrogen embrittlement. On a mild steel (0.18 percent carbon), the results were somewhat better. Of the 15 inhibitors investigated, seven failed completely, four prevented hydrogen embrittlement when used in quantities that greatly exceeded the usually recommended concentration, and the four remaining inhibitors proved to be effective in preventing hydrogen embrittlement when used in the prescribed quantities.

Zapffe and Haslem(14) also investigated the effect of surface-active substances added to acid pickling baths on the hydrogen embrittlement of stainless steel and carbon steel (0.18 percent carbon). Surface-active substances facilitate wetting of the material with the acid, but they do not accelerate the actual pickling process. Generally, they do not have significant inhibiting action, and the inhibiting effect is further reduced with increasing temperature. However, the investigators found that the addition of nonionizing wetting agents resulted in a reduction or prevention of hydrogen embrittlement in the carbon steel. Particularly good results were obtained with polyethylene glycols having a complex molecular structure. The efficiency of these wetting agents increased with their molecular weight. The cation- and anion-sensitive wetting agents investigated in this same work had no effect on the hydrogen embrittlement of the material tested. None of the surface-active agents had any inhibiting effect when pickling stainless steel.

Meyer(15) investigated the effects of 18 inhibitors on hydrogen embrittlement, using a 0.58 percent carbon patented steel wire. He found that only one inhibitor gave substantial protection, but all gave some protection as shown in Tables 1 and 2. In a 15 percent (by weight) H_2SO_4 solution, the protective values ranged from 5 to 87.5 percent, while corresponding values for pickling acid that contained 7.5 percent (by weight) H_2SO_4 and 2.3 lb/gal $FeSO_4 \cdot 7H_2O$ varied between 8.5 and 96 percent. These protective values were based on the number of stress reversals applied to the wire specimens to produce failure. Although the dynamic bend test will indicate severe embrittlement, it is not as sensitive as the sustained-load test for determining susceptibility to hydrogen-stress cracking. The results of this investigation also showed that the inhibiting action of the pickling additive on metal corrosion is in no way related to its inhibiting action on hydrogen embrittlement.

Meyer also evaluated a number of surface-active substances under the same conditions as those used for testing the inhibitors. The substances evaluated were nonionizing wetting agents that were shown by Zapffe and Haslem(14) to exert a beneficial effect in inhibiting hydrogen embrittlement in low-carbon steels. These nonionizing wetting agents had only slight inhibiting effects on hydrogen embrittlement in this steel wire of higher carbon content.

Anderson and associates(16) studied the effect of certain organic inhibitors on the absorption of hydrogen by AISI 1095 steel pickled in 4.8 N HCl. They suggest that the rate of hydrogen entry into the steel and consequent embrittlement might be decreased by affecting the rate of any one of the following reactions: (1) chemisorption of hydrogen on the steel surface, (2) recombination of atomic hydrogen into the molecular form, and (3) removal of chemisorbed hydrogen from the metal surface by reaction with an inhibitor. Their results showed that the quantity of hydrogen taken up by uninhibited acid was neglegible, most of the hydrogen being presented to the steel surface. DHQ*, in the concentrations used, cut the rate of hydrogen evolution by a factor of 50. While it was effective in reducing the total metal attack, it did not appreciably affect the H_2/Fe ratio (millimoles of hydrogen evolved to millimoles of iron simultaneously dissolved). With hexamine, on the other hand, the hydrogen taken up by the inhibitor (and, thus, made unavailable to the steel) increased with the amount of the concentration of the hexamine. A combination of DHQ and hexamine cut the rate of hydrogen evolution by a factor of 200. Enough DHQ in the presence of the hexamine affectively stopped the uptake of hydrogen by the hexamine.

Several studies have been conducted to evaluate the effectiveness of acetylenic alcohols and derivatives for limiting both hydrogen absorption by steel and dissolution of steel during pickling. Although information on the degree of protection of mild steel by acetylenic acid inhibitors is presented in several papers, quantitative information is not given on the hydrogen absorption by steel immersed in acid solutions containing these inhibitors. Hudson and Riedy(17) studied the effectiveness of 16 water-soluble

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*DHQ stands for 6-methyl-3-p-tolyl-3, 4-dihydroquinazoline.

TABLE 1. HYDROGEN EMBRITTLEMENT AND PROTECTIVE VALUES AT 150 F[(15)]

A = 15 percent by weight of sulfuric acid (1.58 lb H_2SO_4/gal).
B = 7.5 per cent by weight of sulfuric acid with 2.3 lb $FeSO_4 \cdot 7H_2O$/gal.

	A		B	
Inhibitor	Stress Reversals (Ultimate Bending Strength)	Hydrogen-Embrittlement Protective Value[(a)], percent	Stress Reversals (Ultimate Bending Strength)	Hydrogen-Embrittlement Protective Value[(a)], percent
Plain acid	5.6	0	7.2	0
Adacid-EB	11.2	87.5	11.6	94.0
Adacid-EN	8.5	45.0	11.1	96.0
Adacid-EN-R	7.2	25.0	8.5	27.0
Adacid-HV	6.4	12.5	8.2	23.0
Adacid-ER	6.6	15.5	8.7	31.5
Adacid-EX	8.3	42.0	10.3	65.0
German product	6.9	20.0	8.2	23.0
German product	7.2	25.0	8.6	29.0
German product	7.1	23.5	9.6	50.0
German product	7.5	30.0	6.7	31.0
German product	8.4	44.0	9.2	41.5
German product	7.9	36.0	9.0	37.5
German product	9.5	61.0	10.0	58.5
German product	5.9	5.0	7.6	8.5
American product	7.3	26.5	9.7	52.0
American product	8.6	47.0	10.2	62.5
American product	7.8	34.0	9.0	37.5
French product	7.9	36.0	8.7	31.0

(a) Hydrogen-embrittlement protective value $= 100 \frac{B_r - B_g}{B_r}$,

where
B_r = loss of stress reversals in plain acid
B_g = loss of stress reversals in inhibited acid.

TABLE 2. METAL CORROSION AND HYDROGEN EMBRITTLEMENT[(15)]

Pickling solution containing 15 percent by weight or 1.58 lb/gal of sulfuric acid at 150 F.

Inhibitor	Metal Corrosion Protective Value[(a)], percent	Hydrogen Embrittlement Protective Value[(b)], percent
Plain acid	0	0
Adacid-EB	94.3	87.5
Adacid-EN	89.5	45.0
Adacid-EN-R	95.0	25.0
Adacid-HV	76.7	12.5
Adacid-ER	88.8	15.5
Adacid-EX	82.2	42.0
German product	82.5	20.0
German product	71.5	25.0
German product	85.0	23.5
German product	47.5	30.0
German product	76.5	44.0
German product	76.2	32.0
German product	85.0	61.0
German product	76.6	5.0
American product	70.5	26.5
American product	87.5	47.0
American product	94.5	34.0
French product	72.5	36.0

(a) Corrosion protective value $= 100 \frac{V_r - V_g}{V_r}$,

where
V_r = loss of iron in plain acid
V_g = loss of iron in inhibited acid.

(b) Hydrogen-embrittlement protective value $= 100 \frac{B_r - B_g}{B_r}$

where
B_r = loss of stress reversals in plain acid
B_g = loss of stress reversals in inhibited acid.

acetylenic compounds and two commercial inhibitors used in 2N sulfuric acid at 100 F. Ten acetylenic alcohols and six acetylenic diols were studied. The effectiveness of these compounds was determined by measuring the metal loss and the amount of hydrogen absorbed (warm-extraction method) for a low-carbon steel immersed in these solutions for either 4 or 24 hours. 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. Most of the acetylenic inhibitors that were effective at 100 F also were effective at 180 F. Commercial inhibitors, however, were not nearly so effective in limiting hydrogen absorption at the higher temperature as they were at 100 F (Table 3).

The mechanism by which organic inhibitors reduce attack and limit hydrogen absorption is still not definitely known. It is believed that the polar atoms of nitrogen and sulfur serve to attach the molecules to the metal surface at points where otherwise some essential step in the corrosion process would occur. Generally, the efficiency of inhibitors increases as the length and number of side chains attached to the polar atom increase. However, some small molecules, such as formaldehyde, can act as inhibitors. Most of the present effective inhibitors interfere mainly with the anodic reaction, although the cathodic reaction also is usually retarded somewhat.

Although certain inhibitors have been shown to be effective in reducing the absorption of hydrogen by steel during acid pickling, it is best to avoid pickling and all cathodic cleaning processes altogether for high-strength steels, which are especially susceptible to hydrogen-stress cracking. For these materials, scale is best removed mechanically, and only alkaline or anodic cleaning processes should be used.

ELECTROPLATING PROCESSES TO MINIMIZE HYDROGEN EMBRITTLEMENT OF ULTRAHIGH-STRENGTH STEELS

Electroplating of metallic materials is done for a variety of reasons, including ornamentation, protection against corrosion, building up of worn parts, improving wear resistance, improving light reflectance, or otherwise changing the physical and chemical properties of the surfaces being plated. The most common reason for electroplating high-strength steel parts used in the aircraft and aerospace industries is for protection against corrosion. However, the application of electrodeposited coatings to solve corrosion problems can make the part susceptible to failure by another mechanism, namely, hydrogen-stress cracking.

Cadmium Electroplating

Cadmium electroplates on steel parts have been used extensively in the aircraft industry to provide galvanic protection against corrosion. However, cadmium plating 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

TABLE 3. EFFECTIVENESS OF PICKLING INHIBITORS IN 2N SULFURIC ACID AT 100 AND AT 180 F FOR 4-HOUR IMMERSION TIME(17)

Inhibitor	Inhibitor Concentration	Weight Loss, mg/cm^2		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	0.05 M	0.4	11.7	98	95	1.0	3.1	88	86
1-Pentyn-3-ol	0.05 M	0.2	2.3	99	99	1.0	1.2	88	95
1-Hexyn-3-ol	0.05 M	0.2	3.2	99	99	1.2	0.3	85	99
4-Methyl-1-pentyn-3-ol	0.05 M	0.2	4.9	99	98	0.9	0.5	89	98
1-Ethynylcyclohexan-1-ol	0.05 M	0.4	1.9	98	99	0.7	0.3	92	99.9
2-Butyn-1,4-diol	0.05 M	0.4	7.0	98	97	1.4	3.1	83	86
3,6-Dimethyl-4-octyn-3,6-diol	0.05 M	0.6	164.4	97	24	0.9	19.5	89	12
3-Methyl-1-pentyn-3-ol	0.05 M	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

protection than cadmium electroplating. Consequently, considerable effort has been expended in trying to develop cadmium-electroplating processes that are nonhydrogen-embrittling that would 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 thin, porous plates at high current densities. The porous plates would facilitate the 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 no ionizable hydrogen.

The following paragraphs describe the results of a number of these investigations.

A cooperative testing program (Project 6-61) was conducted by the Aerospace Research and Testing Committee(18) to compare the hydrogen-embrittlement characteristics of several electroplating systems that were reported to be nonembrittling. The plating processes were evaluated by sustained-load tests employing notched tensile specimens (0.003-inch notch root radius) and Douglas ring specimens made of AISI 4340 steel (280-ksi tensile strength).

The results of the tests employing the Douglas ring specimens were inconclusive, as these specimens were not sufficiently sensitive to detect embrittlement except in the cases of severe embrittlement. The results of the tests employing the notched tensile specimens were as follows (the lower critical stress* is shown in parentheses):

(1) Triethanolamine (260,000 psi) and Boeing BAC 5718 high-efficiency bath (270,000 psi). Very little embrittlement shown. Lower critical stress approximately 10,000 psi below upper critical stress. The triethanolamine system employs no baking treatment, while the Boeing BAC 5718 process employs a 23-hour bake at 375 F.

(2) Lockheed PS 491 g Type II Class C (245,000 psi) and Douglas K.2 Cyanide (225,000 psi). Only slightly more embrittlement shown than the processes listed under (1). The Lockheed process employs an 8-hour bake at 375 F, while the Douglas process is followed by a 23-hour bake at 395 F. Although the Dalic brush plating appeared to be in this class, there were not sufficient data to prove this.

(3) Cleveland Pneumatic Tool, CPT 8206 (215,000 psi). This process is followed by a 23-hour bake at 380 F to 400 F.

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*The lower critical stress is defined as the maximum stress to which the specimen can be loaded without producing failure.

(4) The remaining plating systems showed lower critical stresses in the range from 185,000 psi to 65,000 psi, as follows:

Titanium cadmium plating (185,000 psi), baked 12 hours at 375 F

Grumman nonaqueous plating, dimethylformamide (175,000 psi), no bake

Lockheed Type II Class B (110,000 psi), no bake

Douglas fluoborate (65,000 psi), baked 23 hours at 395 F, bath contained brightener.

In both the titanium-cadmium plating process and the Douglas fluoborate process, the specimens were stripped after initial plating and were replated. It was not known if this procedure was responsible for the lower values of lower critical stress obtained from these systems; however, it was suspected that it had an influence on them.

More recent investigations of the titanium-cadmium, and the Grumman dimethylformamide electroplating processes, which will be discussed in subsequent sections, have shown these processes to be essentially nonembrittling.

Of the five least-embrittling plating systems (Groups 1, 2, and 3), one was an organic system (triethanolamine solution). The remaining four systems involved plating at high current densities (50 to 70 asf), and none of the baths contained brighteners. These plating conditions would be expected to produce porous deposits that would facilitate hydrogen removal during the indicated baking treatments employed after plating. Also, only one of these processes, the Lockheed PS 491 g, Type II, Class C employed an acid etch prior to plating. All the other processes utilized abrasive cleaning prior to electroplating.

As was discussed in the previous review of the literature(1), other investigators(19,20) have shown that cadmium deposits from high-efficiency cyanide baths without brighteners, and cadmium plates deposited 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 is questionable. When brighteners are added to these baths to produce smooth, bright, fine-grained deposits, the specimens are embrittled even after receiving the baking treatment, as is shown in Table 4. Therefore, even though porous plates can minimize hydrogen embrittlement, they are not desired 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 conventional cyanide-cadmium processes. The cadmium fluoborate bath operates at nearly 100 percent plating efficiency and, since hydrogen evolution is inversely related to efficiency, very little if any hydrogen is evolved. As a result, much less hydrogen is available to enter the steel during fluoborate-cadmium plating compared to conventional cyanide-cadmium plating (conventional cyanide baths are about 85 percent efficient at a current density of 25 asf). Devanathan, Stachurski, and Beck(21), who measured the quantity of hydrogen permeating thin membranes of Armco

TABLE 4. RESULTS OF SUSTAINED-LOAD TESTS EMPLOYING NOTCHED TENSILE SPECIMENS CADMIUM PLATED FROM HIGH-EFFICIENCY BATHS WITH AND WITHOUT BRIGHTENERS

Material	Ultimate Tensile-Strength Range, ksi	Tensile Strength of Unplated Notched Bar, ksi	Plating Bath(a)	Current Density, asf	Baking Treatment	Applied Stress, percent NTS	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	19
AISI 4340	260-280	360, $K_t = 3.2$	H. E. Bright Cad.	20	23 hr at 375 F	75	26	3 of 3	19
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	19
AMS 6427	220-240	330, $K_t = 3.2$	H. E. Cad.	20	23 hr at 375 F	75	150	0 of 2	19
AISI 4340	260-280	360, $K_t = 3.2$	H. E. Cad.	20	23 hr at 375 F	75	140	3 of 3	19
AISI 4340	260-280	360, $K_t = 3.2$	H. E. Cad.	40	23 hr at 375 F	75-90	200	0 of 16	19
AISI 4340	290	435, $K_t = 2$	H. E. Cad.	36	23 hr at 375 F	69	694	0 of 3	20
AISI 4340	290	435, $K_t = 2$	H. E. Bright Cad.	36	23 hr at 375 F	69	33	1 of 1	20

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

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

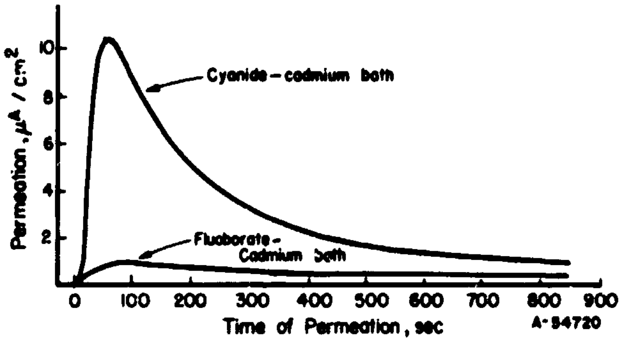
ingot iron during various electroplating processes, demonstrated that hydrogen absorption by the iron was much lower for fluoborate plating than for the cyanide process. Their results are shown in Figure 1. By integrating the area under the curves, they obtained the total quantity of hydrogen that permeated each membrane. These values are presented in Table 5. As can be seen from these results, the fluoborate plating process introduced significantly less hydrogen than did the cyanide plating process. This behavior was attributed to the low steady-state hydrogen coverage from the fluoborate bath. It is also interesting to note the initial steep rise in hydrogen permeation, particularly from the cyanide-cadmium bath, and then the decrease in permeation. The initial steep rise in permeation from the cyanide bath was attributed to the high hydrogen coverage and the effect of the CN^- ion on the recombination rate of hydrogen atoms to form molecules, as CN^- has been shown to effectively retard recombination. The decrease in hydrogen permeation with increased plating time was explained by the barrier effect of the cadmium layer after a critical thickness was deposited.

Fannin(22) evaluated the hydrogen-embrittling tendencies of the cadmium fluoborate process using the sustained-load tests with notched tensile specimens of AISI 4340 steel heat treated to the 220 to 240-ksi strength level. All the cadmium fluoborate specimens survived applied stresses of 75 percent of the notched-bar tensile strength of unplated specimens for 100 hours. However, when the stress was increased to 90 percent of the notched-bar tensile strength, four of six specimens that had not been baked after plating failed in less than 50 hours. Only one of the specimens baked for 3 hours at 375 F, and one baked for 24 hours at 375 F failed at this higher stress level. For the specimens with no bake and those with a 3-hour bake, the performance in the sustained-load test was significantly better than specimens receiving the same postplating processing after conventional cyanide-cadmium electroplating.

Forney and Katlin(23) also showed the superiority of cadmium fluoborate plating over cyanide-cadmium plating using half-ring specimens of AISI 4340 steel heat treated to the 230-ksi and 270-ksi strength levels. Again the specimens plated in the fluoborate bath were initially less embrittled, and embrittlement relief was more readily achieved than specimens plated in cyanide bath. Geyer, Lawless, and Cohen(20) obtained similar results in evaluating the cadmium fluoborate bath with various additions to change the porosity of the deposit. These investigators used sustained-load tests employing notched tensile specimens of AISI 4340 steel heat treated to the 290-ksi strength level (notched-bar tensile strength = 435 ksi). The criterion used for acceptance of a plating system as being nonhydrogen embrittling was that four of four specimens withstand an applied stress of 300 ksi for the duration of the test. In no case did the cadmium fluoborate specimens (baked 23 hours at 375 F) meet this criterion, even though they showed less embrittlement than did conventional cyanide-cadmium-plated AISI 4340 steel specimens.

These investigators also evaluated the susceptibility of SAE H-11 steel (280-ksi strength level) to hydrogen embrittlement induced by electroplating in a cadmium fluoborate bath. This steel showed no detrimental embrittlement after plating and baking for 23 hours at 375 F. This behavior was attributed to the reduced susceptibility of the H-11 steel to hydrogen embrittlement.

Dougherty(24) reported an interesting result obtained during his evaluation of the cadmium fluoborate process employing a bath that contained a brightener. Although the AISI 4140 and AISI 4340 steel specimens plated in the fluoborate bath were embrittled only about one-fourth as much as were the specimens plated in the cyanide-cadmium bath, complete, or practically complete embrittlement relief could not be obtained with



Thickness of Membrane = 0. 77 mm
Current Density = 8. 1 ma/cm^2

FIGURE 1. PERMEATION OF THIN ARMCO IRON MEMBRANE BY HYDROGEN DURING ELECTRODEPOSITION OF CADMIUM FROM CYANIDE AND FLUOBORATE BATHS(21)

Permeation units are microamperes per square centimeter, the current in the anode circuit at the exit surface of the iron membrane.

TABLE 5. QUANTITY OF HYDROGEN PERMEATING ARMCO IRON MEMBRANES DURING ELECTRODEPOSITION OF CADMIUM FROM CYANIDE AND FLUOBORATE BATHS(21)

Number of Curve in Figure 1	Electroplating Bath	Quantity of Hydrogen Permeated, 10^{-9} moles/cm^2 In 0-400 Seconds	In 400-800 Seconds	In 0-800 Seconds
1	Cyanide	21. 46	5. 92	27. 38
2	Fluoborate	2. 66	1. 77	4. 33

fluoborate cadmium-plated specimens. In fact, specimens baked for 2 and 4 hours at 375 F showed more embrittlement than did the as-plated specimens. No explanation was given for this unexpected behavior.

Dougherty pointed out that the fluoborate cadmium plating shows a distinct advantage over cyanide cadmium for plating of parts that contain high residual tensile stresses on the surface or surfaces to be plated. However, when the fluoborate cadmium process is used, baking treatments should be extended to more than 4 hours at 375 F.

Although the cadmium fluoborate bath 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. Therefore, electroplaters prefer the cyanide-cadmium bath.

In 1957, investigators at Case Institute of Technology developed a new hydrogen-embrittlement recovery treatment(25,26). The procedure was as follows: A thin layer of cadmium (0.125 mil thick) was deposited on the steel from a cyanide bath containing a brightener. The specimen was then baked to full recovery (1 hour at 300 F). Finally, a second layer of cadmium was deposited to obtain the desired plate thickness. The investigators reported no embrittlement after the second plating and attributed this behavior to the barrier effect on hydrogen entry of the initial thin cadmium plate. They also reported that this technique was so efficient that no baking treatment was required after the second electroplating operation. However, their criterion for embrittlement relief was restoration of original ductility as measured in a conventional test. Satisfaction of this criterion does not ensure freedom from hydrogen-stress cracking in a sustained-load test.

Several other investigations of this technique conducted more recently have produced contradictory results. Micillo(27) tested C-ring specimens of AISI 4340 steel and AMS 6427 (AISI 4330 M) steel (220-ksi and 215-ksi yield strengths, respectively) that had been plated with a 0.1-mil layer of cadmium from cyanide baths with and without brighteners, baked 1 hour at 375 F, than overplated to a total plate thickness of 0.5 mil of cadmium. Prior to testing, the specimens were baked 23 hours at 375 F. All the specimens survived 646 hours at stresses equal to 90 per cent of their yield strengths.

However, Forney and Katlin(23) evaluated this technique using a half-ring compression test employing AISI 4340 steel with an initial thin cadmium plate deposited from a cyanide bath without a brightener and subsequently baked to full recovery. They found that overplating the initial thin deposit with cadmium produced significant embrittlement as measured by reduction in breaking load and deflection at failure. When the initial thin cadmium plate was overplated with chromium, the embrittlement was even more severe. Obviously, in their experiment, the thin cadmium preplate deposited from a cyanide bath without a brightener did not act as a barrier to hydrogen entry into the steel.

Dougherty(24) also evaluated the barrier effect of a thin cadmium electroplate to hydrogen embrittlement resulting from subsequent cadmium overplating using half-ring specimens of AISI 4140 steel and AISI 4340 steel both heat treated to strength levels of 260 ksi and 285 ksi. The specimens were initially plated with 0.125 mil of cadmium from cyanide baths with and without a brightener and then were baked for 2 hours at 325 F. As preplated and baked, these specimens showed losses of ductility (as measured by deflection at fracture) ranging from 8 to 18 percent, except for the AISI 4340 specimens at the 285-ksi strength level, which showed a loss of only 4 percent. (These latter specimens were not embrittled significantly, even when no barrier preplate was used.) No appreciable decreases in ductility or strength occurred as a result of overplating a bright preplate, but the porous preplate (without brightener) allowed hydrogen to penetrate and, except for the AISI 4340 steel at the 285-ksi strength level, cause significant embrittlement as shown in Figure 2.

Dougherty suggested the following process as an alternate to the conventional one-step electroplating process:

(1) Plate to 0.125 mil from a cyanide cadmium bath containing a brightener
(2) Bake for 2 to 4 hours at 375 F
(3) Overplate to 0.5 mil to obtain a bright, fine-grained finish.

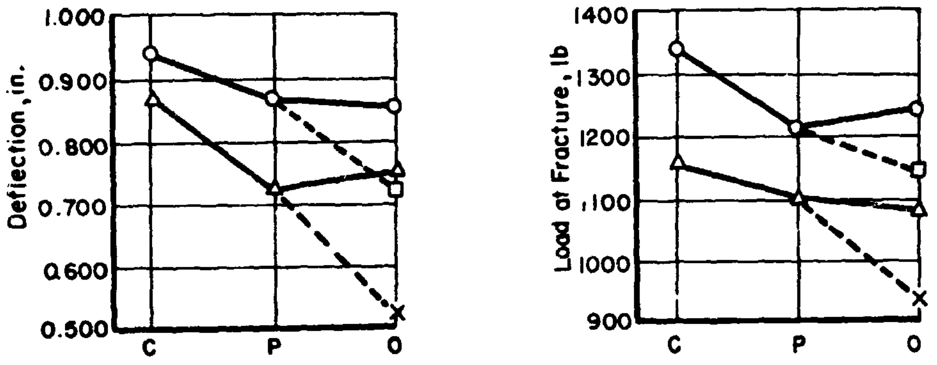
This duplex plating procedure should have the added advantage of making any porosity network that might exist in the deposit discontinuous, thus increasing the corrosion resistance.

It appears from the results of these investigations that a thin (0.125 mil thick), bright-cadmium electroplate baked to full recovery acts as an effective barrier to hydrogen penetration during subsequent overplating. However, a dull (porous) preplate is not an effective barrier, and significant embrittlement can result from hydrogen introduced into the steel in the overplating operation.

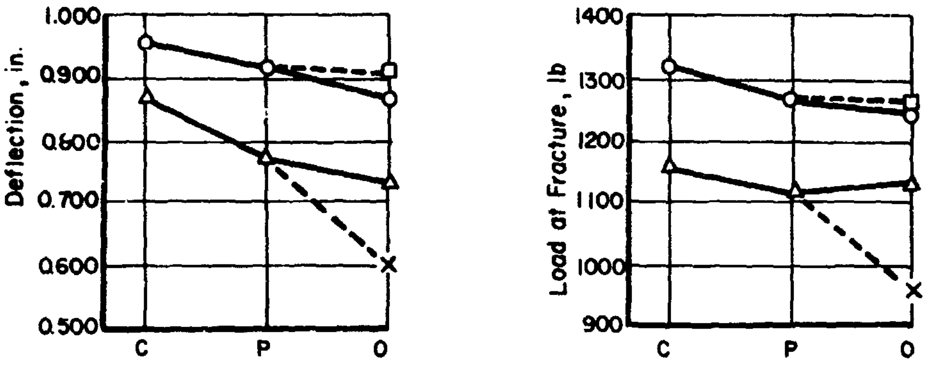
Thin undercoats of copper and nickel also have been investigated to determine their effectiveness in preventing hydrogen embrittlement. Beck and Jankowsky(28) investigated the effectiveness of Watts-type bright nickel and pyrophosphate copper undercoats (both electroplated coatings) in minimizing embrittlement induced by overplating with cyanide cadmium and conventional chromium electroplates, both of which have been shown to severely embrittle ultrahigh-strength steels. Their results indicated that, regardless of the metal that forms the undercoat or the plate deposited on it, the protection against hydrogen embrittlement provided by the undercoat usually increases with its thickness, as is shown in Figure 3. When the undercoat becomes thick enough, overplating no longer induces additional embrittlement, and the reduction in ductility as measured by reduction in deflection at failure remains the same as it was for the undercoat alone.

Results of tensile tests of specimens with copper and nickel undercoats overplated with cyanide cadmium are shown in Figure 4. It is shown that there is a minimum thickness of undercoat that must be exceeded before the beneficial effect of the undercoat is obtained. Also, the ductility of the specimens increased rapidly with increased undercoat thickness, until the ductility (reduction in area) of the specimen plated with copper or nickel alone is achieved.

More sensitive sustained-load tensile tests indicated less beneficial effect of the undercoats in minimizing hydrogen embrittlement than did the other two methods; this behavior is shown in Figures 5 and 6. The investigators concluded that the thin nickel and copper metallic undercoats offered some protection against hydrogen embrittlement resulting from subsequent overplating with cyanide cadmium or chromium, and that this protection resulted from the barrier effect of the coatings to hydrogen diffusion. Barrier effectiveness is apparently related to the thickness of the undercoat. The



a. 4140 Steel



b. 4340 Steel

A-54724

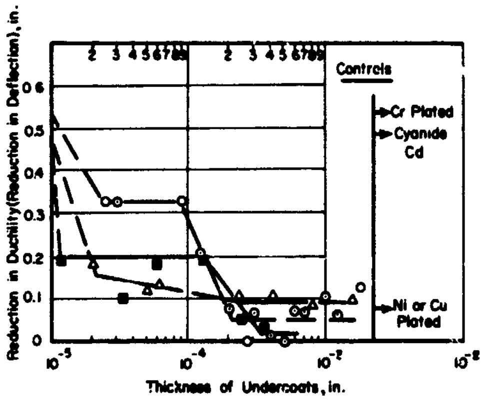
——○—— Preplate with brightener
----□---- Preplate without brightener

——△—— Preplate with brightener
----×---- Preplate without brightener

○, □ 425 F temper
×, △ 550 F temper

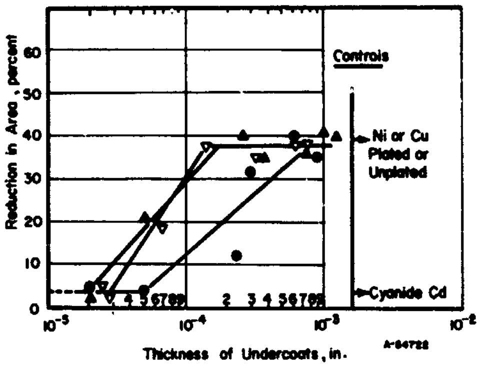
C = Control specimen
P = Preplated specimen
O = Overplated specimen

FIGURE 2. DATA SHOWING THE BARRIER EFFECT OF THIN CADMIUM ELECTROPLATES DEPOSITED FROM CYANIDE BATHS WITH AND WITHOUT BRIGHTENERS ON HYDROGEN EMBRITTLEMENT CAUSED BY OVERPLATING WITH CADMIUM(24)



■ Pyrophosphate copper, overplated with cyanide cadmium
⊙ Pyrophosphate copper, overplated with chromium
△ Bright Watts nickel overplated with cyanide cadmium

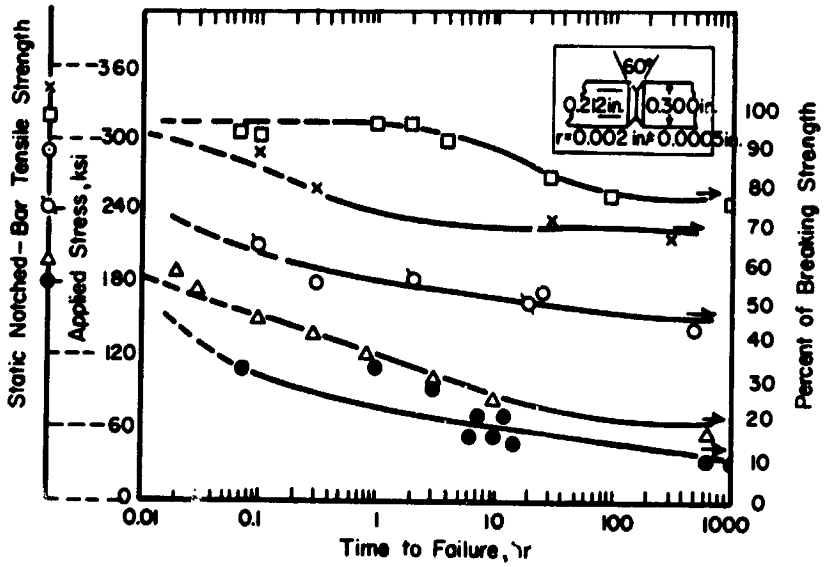
FIGURE 3. THE EFFECT OF THICKNESS OF COPPER AND NICKEL UNDERCOATS OVERPLATED WITH CYANIDE CADMIUM OR CHROMIUM ON BEND DUCTILITY(28)



▽ Pyrophosphate copper undercoat
▲ Bright Watts nickel undercoat
● Sulfamate nickel undercoat

FIGURE 4. THE EFFECT OF COPPER AND NICKEL UNDERCOATS OVERPLATED WITH CYANIDE CADMIUM ON TENSILE DUCTILITY(28)

Reduction in Area on 0.505-in.-diam Tensile Bars
Rate of cross-head travel from yield to ultimate = 0.1 in./min.
Strain rate to yield maintained at 0.05 in./in./min.

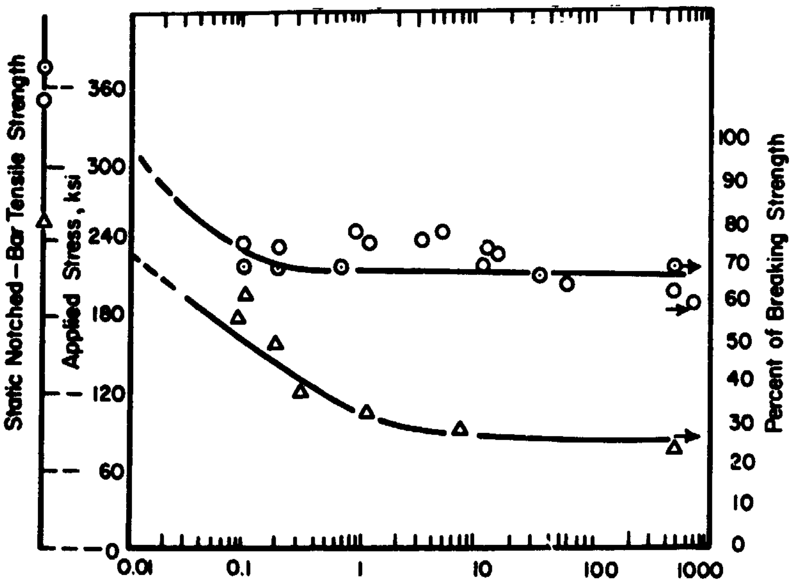


Plated with: □ Fluoborate cadmium - Avg thickness 2 x 10^{-4} in.
× Pyrophosphate copper - Avg thickness 5 x 10^{-4} in.
○ Pyrophosphate copper - Avg thickness 5 x 10^{-4} in.; Overplated with Cr - Avg thickness 1 x 10^{-3} in.
Q Pyrophosphate copper - Avg thickness 1.5 x 10^{-4} in.; Overplated with Cr - Avg thickness 1 x 10^{-3} in.
△ Cyanide-cadmium plated - Avg thickness 2 x 10^{-4} in.
● Chromium plated - Avg thickness 1 x 10^{-3} in.

All thicknesses taken at base of notch.

FIGURE 5. RESULTS OF STATIC-LOADING TESTS OF CYLINDRICAL NOTCHED TENSILE SPECIMENS, SHOWING THE BARRIER EFFECT AGAINST HYDROGEN OF A PYROPHOSPHATE COPPER UNDERCOAT(28)

Geometric Stress-Concentration Factor = 6.0.



Plated with: ⊙ Bright Watts Ni plated - Avg thickness 5 x 10^{-4} in.; Overplated with cyanide cadmium - Avg thickness 2 x 10^{-4} in.
○ Bright Watts Ni plated - Avg thickness 5 x 10^{-4} in.
△ Cyanide-cadmium plated - Avg thickness 2 x 10^{-4} in.

All thicknesses taken at base of notch.

FIGURE 6. RESULTS OF STATIC-LOADING TESTS OF CYLINDRICAL NOTCHED TENSILE SPECIMENS SHOWING THE BARRIER EFFECT AGAINST HYDROGEN OF A BRIGHT WATTS-NICKEL UNDERCOAT(28)

Geometric Stress-Concentration Factor = 4.2

deficiencies in the barrier effectiveness of the coatings, as revealed by the sensitive delayed-failure tests, were attributed to plating imperfections.

Later, the effects of pyrophosphate copper and Watts-type bright nickel as undercoats for cyanide-cadmium plating were reevaluated(24). In this study, the undercoats were plated to a thickness of 0.5 mil, which, according to the previous investigation, was sufficient to act as an effective barrier to entry of hydrogen into the base metal. The undercoats were then overplated with 0.5 mil of cadmium from the embrittling cyanide bath. No baking was applied after either electroplating process. Also, a copper strike was applied to the specimen prior to the pyrophosphate copper deposit.

Although neither type of undercoat completely eliminated embrittlement, both reduced that resulting from cyanide-cadmium plating. From the results of the tests, it appeared that pyrophosphate copper was more effective in reducing hydrogen entry into the steel than was the bright nickel. The author suggested that the undercoats may have acted as effective barriers to hydrogen entry and that the embrittlement observed resulted from the supposedly nonembrittling undercoats themselves and that this possibility justifies further investigation. He concluded that at the present time metallic undercoats promise no particular advantage over straight, or barrier, cadmium plating.

Forney and Katlin(23) showed that thin electroless-nickel barrier plates deposited from both alkaline and acid baths did not prove effective in preventing hydrogen embrittlement of AISI 4340 half-ring specimens when overplated with cadmium from a cyanide bath. The nickel barrier plates were 0.16 mil thick, and the total thickness after cadmium plating was 0.5 mil.

One reportedly low-hydrogen-embrittling process that has received considerable study is the cadmium-titanium (Delta) process, which 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 supension in the plating system(29,30). 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.(29,30) 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(31).

Possible explanations for these observations are that the titanium, which had a greater affinity for hydrogen than does steel, reacts with the hydrogen evolved at the cathode (workpiece) during the plating process and forms a stable hydride, leaving less hydrogen available to enter the steel.(29,30,31) Also, the 0.1 to 0.5 percent titanium codeposited with the cadmium in the electroplate could act as a hydrogen scavenger during the baking treatment and absorb hydrogen that entered the steel during the plating cycle.(29,30,31) This explanation fits the observation that the degree of embrittlement relief increases with increasing plate thickness, in that the increased thickness increases the total available titanium, thereby increasing the scavenging potential(28).

Another significant advantage of the cadmium-titanium alloy 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.(29, 32) The inherent lack of precision of corrosion tests makes it virtually impossible to develop quantitative data on corrosion resistance; however, some investigators have reported no basis-metal corrosion on plated panels after more than 2000 hours of salt-spray exposure. In comparison, conventional cadmium plates have failed within 200 to 500 hours.(29)

In addition, the cadmium-titanium electroplates have shown good adhesion in both bend tests and paint-adhesion tests.(31)

The cadmium-titanium electroplate is deposited by initially applying a cadmium-titanium strike at a cathodic current density of 40 to 45 asf for 15 seconds. Then the current density is reduced to 15 to 30 asf until the desired plating thickness is deposited. At a current density of 30 asf, a 0.0005-inch plate is deposited in about 12 minutes.(29, 31)

Cadmium in the plating bath is supplied as conventional anodes, and titanium is added in the form of a proprietary paste, which is placed on the filter cloth of a continuously operating filter. The titanium content of the bath is usually maintained at approximately 80 ppm by daily additions of hydrogen peroxide to the plating solution. Normally, the bath is operated so that the plate contains between 0.1 and 0.5 percent titanium. This titanium concentration range appears to produce a plate with the most desirable properties. At higher concentrations, the excess titanium appears as a white titanium dioxide powder on the plate surface and does nothing to enhance the plate quality.(29)

The titanium in the plating bath is present in a relatively unstable form, necessitating at least daily analysis and adjustment of the titanium content. This bath is also sensitive to organic and metallic contaminants that act as brighteners. Therefore, only deionized water and high-purity chemicals should be used to prepare the solution. Continuous filtration is required, and the entire bath must be filtered two or three times an hour. Iron has been shown to contaminate the bath and have a severe adverse effect on its performance. It causes spontaneous decomposition of the titanium salt with subsequent loss of perioxide and reduction of the titanium content of the bath and plate. Therefore, the iron concentration in the plating solution must be less than 100 ppm.

Because of the sensitivity of the bath to metallic contaminants, the tank, filter, and associated plumbing should be lined with, or constructed from, a suitably inert material. Also, steel jigs and holding fixtures must be covered with a maskant to avoid contact with the plating solution.

Tables 6 and 7 present the results of several evaluations of the embrittling tendencies and corrosion resistance of the cadmium-titanium electroplating process and resulting electroplates, respectively.

Menasco has used the cadmium-titanium process to electroplate landing gears and many heavy structural components for a commercial jet airliner. Boeing has used this process to electroplate landing struts, flap carriages, and flap tracks for the Boeing 727 jet airliner.

The dimethylformamide (DMF) electroplating bath developed by Grumman Aircraft(35) is a nonaqueous bath and, therefore, does not contain ionizable hydrogen. The cadmium is supplied by cadmium iodide and cadmium anodes.

TABLE 6. RESULTS OF SUSTAINED-LOAD TESTS EMPLOYING NOTCHED TENSILE SPECIMENS OF SEVERAL ULTRAHIGH-STRENGTH STEELS ELECTROPLATED IN THE CADMIUM-TITANIUM BATH

Material	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	33
AISI Type H-11	--[(b)]	330	None	75	1,994	No	33
AISI 4340 Steel	260-280	340	(b)	75	200	No	30
4330 M[(c)]	220-240	334	(b)	75	700	No	30
98BV40	275	338	None	75	0.8	Yes	31
98BV40	275	338	None	75	3.4	Yes	31
98BV40	275	338	24 hr, 375 F	75	58.3	Yes	31
98BV40	275	338	24 hr, 375 F	75	84.7	Yes	31
98BV40	275	338	24 hr, 375 F	75	101.8	No	31
				90	8.4	Yes	31

(a) NTS = notched-bar tensile strength.

(b) Information not provided.

(c) AMS 6427.

TABLE 7. RESULTS OF CORROSION TESTS PERFORMED ON CADMIUM-TITANIUM-PLATED AND CONVENTIONAL CADMIUM-PLATED STEEL PANELS

Base Steel	Electroplate	Plate Thickness, mil	Exposure Conditions	Test Duration, hr	Remarks	Reference
--	Cd-Ti, bright chromate	0.5	ASTM-B-117(a)	2,000	No red rust	32
--	Cd-Ti, bright chromate	0.3	ASTM-B-117(a)	2,000	No red rust	32
--	Cd-Ti, bright chromate	0.5	ASTM-B-368-61T(b)	24	No red rust	32
--	Cd-Ti, bright chromate	0.3	ASTM-B-368-61T(b)	24	No red rust	32
--	Cd-Ti, 68 ppm Ti	0.4	Salt spray	500	No rust	34
--	Cd-Ti, 68 ppm Ti	0.5	Salt spray	500	No rust	34
--	Cd-Ti, 84 ppm Ti	0.5	Salt spray	500	No rust	34
--	Cd-Ti, 84 ppm Ti	0.5	Salt spray	500	No rust	34
--	Cd-Ti, 139 ppm Ti	0.3	Salt spray	500	No rust	34
--	Cd-Ti, 139 ppm Ti	0.4	Salt spray	500	No rust	34
AISI 4130	Cd-Ti	0.45	ASTM B-117-57T(a)	1,390	No rust	33
AISI 4130	Cd-Ti	0.45	ASTM B-117-57T(a)	1,390	No rust	33
AISI 4130	Cd	0.45	ASTM B-117-57T(a)	1,390	No rust, more pitting	33
AISI 4130	Cd	0.45	ASTM B-117-57T(a)	1,390	No rust, more pitting	33

(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.

The results of two investigations employing notched tensile specimens of AISI 4340 steel (260 to 280-ksi strength range) that were electroplated by the DMF process are contradictory. In one study(18), described previously, DMF-plated notched tensile specimens failed in the sustained-load test at applied stresses of 180,000 psi. In the other study(35), 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. In both studies, the specimens were prepared for electroplating by mechanical cleaning, and no postplating baking treatment was employed. For comparison, Micello(35) plated two specimens in a conventional cyanide-cadmium bath. Both of these specimens failed at applied stresses of 75 percent of the notched-bar tensile strength after 13 hours, even though they had been baked for 23 hours at 375 F after plating. It also was reported that the adhesion and corrosion protection obtained with the cadmium deposit from the DMF bath compared favorably with deposits obtained from the aqueous cyanide plating bath.

The differences in the embrittling tendencies of the DMF-cadmium electroplating process observed in these two studies have not been explained. However, it was recommended in the study where embrittlement was apparent that this process be evaluated further, but whether this was done has not been reported.

A selective-plating process that has been reported to be nonhydrogen embrittling was developed recently by Selectrons, Ltd.(36) The Selectron Cadmium LHE process has been reported to permit rapid deposition of cadmium on ultrahigh-strength steels without introducing significant hydrogen embrittlement. Such deposits have fulfilled the requirements of specification QQ-P-416a without being baked after plating.(37) It also has been reported that the corrosion resistance of this cadmium coating was equal to that of conventional cadmium electroplates, if the manufacturer's recommended practices were followed.(37) The Selectron Cadmium LHE process has been approved for selective-plating operations on ultrahigh-strength steels with tensile strengths up to 240 ksi by Douglas Aircraft Company and on steels with tensile strengths up to 280 ksi by Lockheed Aircraft; neither requires subsequent baking treatments.(38)

While the above-mentioned results for the Selectron Cadmium LHE process were obtained with brush- or selective-plating operations, tests have been conducted by the United States Naval Air Station, Alameda, California, on the use of Cadmium LHE solution in a bath. Although no embrittlement data were given, it was reported that diffusion results obtained with a Lawrence hydrogen gage indicated that the hydrogen penetration with Cadmium LHE was approximately 10 percent of that obtained when using the Delta cadmium-titanium process.(38)

Table 8 presents some of the results of the evaluation of the Cadmium LHE process reported by Jankowsky.(37)

This process has been used to repair-plate a large P-3A main landing gear component, originally vacuum cadmium plated, made from an ultrahigh-strength steel (260 to 280-ksi tensile strength) by the U. S. Naval Air Station, Alameda, California.(39)

Nickel Plating

Nickel electroplates with various properties are applied to metal parts for a variety of reasons. General-purpose nickel plates produced by Watts, sulfamate, and

TABLE 8. RESULTS OF TESTS WITH NOTCHED C-RING SPECIMENS TO EVALUATE THE HYDROGEN-EMBRITTLEMENT TENDENCIES OF VARIOUS SELECTRON CADMIUM-PLATING PROCESSES(37)

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

Process	Applied Stress, percent NTS[a]	Time for Failure
A. Results With Rings Stressed After Plating		
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[b]
Selectron Type LHE	82	40 hr[b]
Selectron Type LHE	75	200 hr[b]
Selectron Type LHE	75	200 hr[b]
Conventional Cyanide Cd	82	Failed on loading
Conventional Cyanide Cd	82	Failed on loading
B. Results With Prestressed Rings		
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[b]
Selectron Type LHE	50	72 hr[b]
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.

fluoborate baths are used primarily to protect iron, copper, and zinc alloys from atmospheric corrosion; to a lesser extent they are used also for decorative purposes. Heavy deposits from the Watts bath are employed to build up worn or undersized parts and to provide protection against corrosive chemical environments. Special-purpose nickel deposits are selected either because of an unusual property of the deposit, such as extreme hardness, or because the plating bath is particularly suited for a special application, such as barrel plating. Black-nickel deposits, derived from baths containing zinc sulfate or zinc chloride, have little protective value and are used primarily to obtain a dark, nonreflective, decorative finish. Bright-nickel deposits are used primarily to provide decorative finishes on metals that, without suitable protection, will corrode or tarnish. These deposits contain various amounts (0.02 to 0.13 percent) of sulfur, which reduces their corrosion resistance. They are applied most frequently as undercoatings for chromium or one of the precious metals or as overcoatings for a sulfur-free nickel deposit (a combination known as "duplex" nickel).(2)

In spite of many reasons for nickel electroplating, very little information on the embrittling tendencies of the various nickel-electroplating baths is contained in the recent literature.

Bergstedt and his associates(40) evaluated the embrittling tendencies of a Watts-nickel plating bath using specimens of H-11 tool steel heat treated to an ultimate tensile strength of 248 ksi. They used loss of ductility, as determined in a conventional tensile test, as the measure of embrittlement. Their results showed negligible change in the percent elongation or reduction of area of the specimens electroplated in the Watts-nickel-plating bath. However, these properties do not provide a very sensitive measure of hydrogen-stress cracking tendency.

As was pointed out in the section on barrier plating, Watts-type-nickel and bright-nickel electroplates have been used as undercoats in attempts to minimize hydrogen embrittlement resulting from conventional cyanide-cadmium plating.(24,28) In one of these studies(24), the investigator suggested the possibility that embrittlement detected in the specimens may have resulted from the electrodeposition of the barrier undercoats rather than from the cadmium overplate.

Probert and Rollinson(41), while attempting to determine effective hydrogen-embrittlement-relief treatments for Watts-nickel-plated specimens, found that the original fracture angle in a bend test could not be restored with any of the selected treatments investigated. However, they gave no details as to the extent of embrittlement induced by the nickel-plating process.

It is pointed out in Volume II of the Metals Handbook(2) that nickel electroplating can cause hydrogen embrittlement in steels, particularly those processed to strength levels above 160,000 psi. To minimize hydrogen pickup, nonembrittling cleaning processes should be employed and, if acid-dip activation treatments are used, immersion times should be held to a minimum. Nickel plating in baths at the high end of the pH range also helps to reduce hydrogen pickup. It is also pointed out that nickel is quite permeable to hydrogen, and, therefore, hydrogen embrittlement can be readily relieved by baking nickel-plated steel parts at moderate temperatures for relatively short periods of time.

DiBari(42) showed that SAE 4340 steel (tensile strength of notched bars = 235 ksi) was embrittled by nickel electroplating. Prior to nickel plating, one set of specimens was activated by an anodic treatment in a 25 percent by weight sulfuric acid bath, while another set was similarly treated in the sulfuric acid bath and then given a nickel strike in an acid nickel chloride bath. Nickel plating after either activating method reduced the tensile strength of noched bars by about 25 percent. The lower critical stress for failure was about 50 percent of the normal noched-bar tensile strength when the anodic sulfuric acid etch was used, and this was reduced further by "striking" in the acid nickel chloride bath. These specimens were subjected to delayed-failure type tests to provide data for comparison with maraging steel.

The 18Ni maraging steel specimens (notched-bar tensile strength = 370 to 385 ksi) were nickel plated after receiving either the anodic sulfuric acid etch or a three-step activation process, that consisted of:

(1) Anodic etching in 25 percent by weight H_2SO_4 for 2 minutes

(2) Immersion in chromic-sulfuric acid (CrO_3, 50 g/l; H_2SO_4, 20 ml/l) for 1 minute; water rinse

(3) Immersion in acid nickel chloride bath for 1 minute, then nickel striking for 1 minute.

Essentially no hydrogen embrittlement resulted. The plating had little or no effect on the tensile-strength values obtained for notched bars, and four nickel-plated notched-tensile specimens survived applied stresses of 90 and 92 percent of the tensile strength of unplated notched specimens for times from 166 to 362 hours without failure.

When a 1-mil chromium electroplate was applied to a nickel-plated (0.5 mil) specimen that had survived a static load of 90 percent of the normal notched-bar tensile strength for over 300 hours, the specimen failed on loading at 81 percent of the notched-bar tensile strength. Similar nickel/chromium-plated specimens that were baked at 450 F for 24 hours prior to testing survived loads of 90 percent of the notched-bar tensile strength for more than 150 hours without rupturing.

Hard-Chromium Plating

Hard-chromium plating, also known as industrial or engineering chromium plating, is used primarily to restore mismachined or worn surfaces and to improve wear, abrasion, heat, and, to a lesser extent, corrosion resistance. For these applications, the plating thickness generally ranges from 0.1 to 20 mils, but for some applications even thicker plates are deposited. Although the chromium plates are quite heavy and are more likely to be impervious than are decorative chromium plates, they do contain microcracks.(2) This condition appears to be quite important from the standpoint of hydrogen embrittlement.

Several investigators have evaluated the hydrogen-embrittlement tendencies of conventional chromic acid-sulfate chromium-electroplating baths.(19,23,24,40-43) The results obtained from these various investigations were quite consistent in that all steels with tensile strengths above about 200 ksi were susceptible to hydrogen-stress cracking and that the severity of embrittlement increased with increasing strength level. Also, several of these investigations revealed that, for a given steel at a given strength level, where it was susceptible to hydrogen embrittlement resulting from chromium electroplating, the chromium bath was much more embrittling than was the cyanide-cadmium bath.(23, 24, 41) Because of this behavior, it is strongly recommended that all parts be stress relieved prior to hard-chromium electroplating.(24)

Although conventional hard-chromium electroplating has been shown to cause severe embrittlement in ultrahigh-strength steel in every investigation reported, it has been shown that embrittlement relief is readily obtained by simple bake-out treatments.(19,23,24,40,41,43) One advantage of chromium electroplates is that they can be baked at significantly higher temperatures than can be used with cadmium electroplates, provided these higher temperatures do not cause degradation of the base metal. As a result, when higher baking temperatures are employed, the baking time can be reduced.

In an evaluation of crack-free chromium plates deposited from the CF-500 bath developed by Metal and Thermit Corporation and conventional (microcracked) chromium electroplates, investigators at Convair reported that the embrittling tendencies of the two electroplates were the same.(44) Sheet specimens of Thermold A (similar to H-11) (NTS = 220 ksi) electroplated with 2 mils of chromium from both baths failed on loading to an applied stress of 200 ksi. However, while a 23-hour bake at 375 F effectively relieved the hydrogen embrittlement from the conventionally chromium-plated specimens, this relief treatment was not adequate for the crack-free chromium-plated specimens, as all the specimens failed the 1000-hour sustained-load test. It was determined that baking at 500 F for 2 hours relieved the embrittlement from the crack-free deposits; however, the investigators recommended a relief treatment of 23 hours at 500 F. The corrosion resistance of the crack-free coating in thicknesses above 2 mils was greater than that of the conventional chromium electroplates of similar thickness.

Table 9 presents data from various investigations showing the embrittling tendencies of chromium-electroplating baths and the effectiveness of baking treatments.

It is apparent from the review of the literature that little work has been directed toward developing nonhydrogen-embrittling chromium-electroplating processes. This may be a reflection on the apparent ease of hydrogen-embrittlement relief with such coatings, or it may be that most steel parts to be chromium plated have strengths below the levels where hydrogen embrittlement becomes significant.

The majority of 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 9. RESULTS OF SUSTAINED-LOAD TESTS EMPLOYING CHROMIUM-PLATED NOTCHED TENSILE SPECIMENS

Material	Ultimate Tensile Strength Level, ksi	Notched-Bar Tensile Strength, ksi	Plating Bath	Baking Treatment	Applied Stress, percent NTS or ksi	Lower Critical Stress, percent NTS	Time for Failure, hr	Number of Specimens Failed at 75 percent NTS	Reference
AISI 4340	260-280	360	Hard chromium	8 hr at 375 F	75	--	125	3 of 8	19
AISI 4340	260-280	360	Hard chromium	23 hr at 375 F	75-95	88	175	0 of 9	19
AMS 6427	220-240	330	Hard chromium	23 hr at 375 F	75-90	88	190	0 of 8	19
4340-1. 5Si	270-300	376	Hard chromium	3 hr at 550 F	75-95	>95	190	0 of 7	19
AISI 4140	270	--	Hard chromium	None	175 ksi	--	<0. 5		23
AISI 4140	270	--	Hard chromium	None	125 ksi	--	<0. 5		23
AISI 4140	270	--	Hard chromium	None	25 ksi	--	<0. 5		23
AISI 4140	270	--	Hard chromium	None	15 ksi	--	>100(a)		23
AISI 4340	220-240	--	Hard chromium	None	75	--	<5	All	43
AISI 4340	220-240	--	Hard chromium	24 hr at 375 F	75 and 90	--	>100	None(b)	43

(a) Specimen did not fail; test discontinued.

(b) No specimens failed at stresses of 90 percent of NTS.

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

HYDROGEN-EMBRITTLEMENT RELIEF TREATMENTS

If hydrogen-stress-cracking failures of high-strength-steel parts are to be prevented, hydrogen must be eliminated from the parts. The ideal way to solve this problem is to prevent hydrogen from entering the steel during all processing operations. However, in most cases that approach is not practicable; therefore, hydrogen that is unavoidably picked up during processing must be removed or put into a nondamaging form.

Hydrogen in steel is quite mobile at ambient temperatures; therefore, in normally dry air, hydrogen is constantly being lost from a piece of ferritic or martensitic steel until the hydrogen content of the steel comes to equilibrium with its environment. The rate of loss depends on, and varies greatly with, such factors as temperature, thickness and shape of part, composition of the steel, whether the steel is ferritic or austenitic, the amount of cold work, the nature of the environment, surface condition, and surface area. Details as to the effects of these variables on hydrogen removal were presented in the report on the initial literature and industrial survey(1) conducted under this contract and will not be presented in the present report.

It has been shown that the rate of hydrogen evolution from all steels increases with increasing temperature, at least within a few hundred degrees of room temperature. Therefore, the most common method of removing hydrogen from steel parts is to bake it out. However, the solubility of hydrogen in alpha-iron increases rapidly with increasing temperature. Therefore, baking or aging treatments to remove hydrogen from ferritic steels must be a compromise between greater permeability or rate of diffusion obtained at higher temperatures (so as to shorten the treatment times) and the lower solubility prevailing at lower temperatures. Frequently a temperature between about 375 F and 400 F is used.

The early investigations of hydrogen embrittlement induced by pickling in acid solutions or by electrolysis showed that aging at room temperature or heating to moderately elevated temperatures caused a gradual recovery of the original ductility. Some investigators reported that complete recovery had been obtained, while others found that recovery was incomplete at either room temperature or at elevated temperatures. However, this early work was done largely with low-carbon steel.

Apparently, low-alloy steels, heat treated to high strength levels, completely recover the ductility lost by hydrogen introduced during acid pickling, provided they are stored for a long time before use, or are baked at a sufficiently high temperature, and provided they are not electroplated after pickling. For example, tensile tests of SAE 4340 steel, heat treated to a hardness of Rockwell C47, indicated that complete recovery of the ductility lost as a result of pickling in hydrochloric acid for 1 hour was accomplished by aging at room temperature for 5 hours or more.(45) Probert and Rollinson(6) showed that embrittlement induced by hydrogen introduced during cathodic cleaning or acid pickling was easily relieved by heating the steel at moderate temperatures for relatively short periods of time. Their results are summarized in Figure 7. They also showed that hydrogen absorbed during cleaning and activation treatments prior

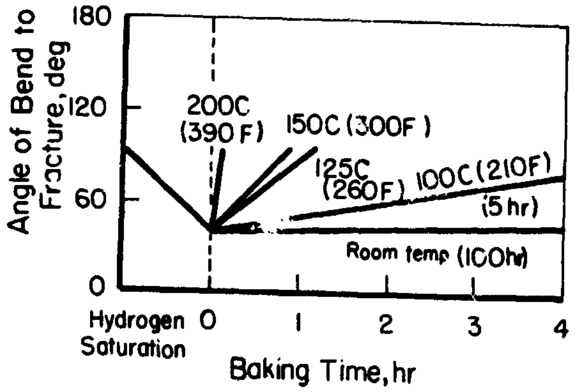


FIGURE 7. REMOVAL OF HYDROGEN EMBRITTLEMENT IN A TOOL STEEL OF HIGH CARBON CONTENT AFTER PICKLING OR CATHODIC CLEANING BUT WITHOUT ELECTROPLATING(6)

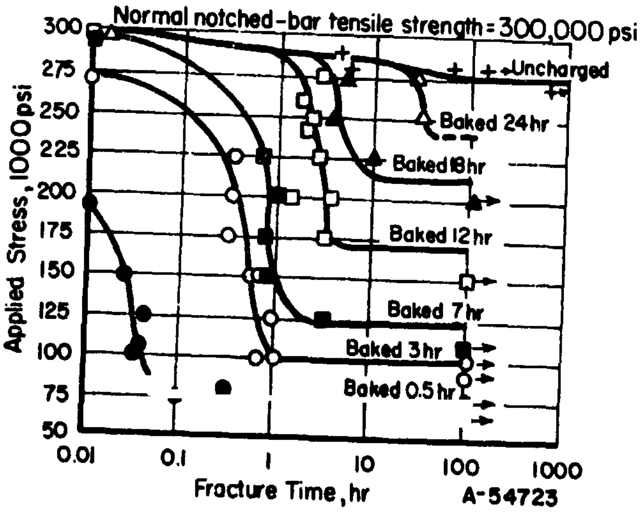


FIGURE 8. STATIC-FATIGUE CURVES FOR VARIOUS HYDROGEN CONCENTRATIONS CORRESPONDING TO DIFFERENT BAKING TIMES AT 300 F AFTER CATHODIC CHARGING(46)

Sharp-notch specimens; 230,000-psi strength level.

to electrolytic or electroless nickel plating was partially removed during the plating operations themselves, presumably because the elevated temperatures of the solutions caused some out-gassing of hydrogen. However, as is shown in Figure 8, other investigators(46) have reported that baking of cathodically charged high-strength steel (300 ksi NTS) specimens for 24 hours at 300 F did not completely eliminate delayed failures at high applied stresses in the more sensitive sustained-load test.

The presence of a more or less impermeable metal coating, such as chromium, cadmium, or zinc, makes the evolution of hydrogen from the base metal more difficult, as is shown in Figures 9 and 10. This behavior may serve to aggravate the effects of embrittlement and delayed failure of electroplated steel. An appropriate baking treatment may restore most or all of the ductility to the plated high-strength steels. However, such a treatment frequently does not overcome the tendency for hydrogen-stress cracking to occur.

Two factors that greatly influence the recovery of properties by baking electroplated high-strength-steel specimens are plate thickness and plate porosity. As was pointed out in the section on electroplating, various investigators(24,26,27) have shown that high-strength-steel parts plated with 0.125 mil of bright cadmium could be baked to full recovery of ductility in relatively short times (1 to 4 hours) at 375 F and replated without further embrittlement.

Chek(47) investigated the influence exerted by variations in the thickness of cadmium plates deposited from a cyanide bath upon recovery from hydrogen embrittlement of AISI 4340 Steel (270-ksi strength level) by baking at 300 F for periods up to 24 hours. Two procedures were used for the detection and evaluation of hydrogen embrittlement – tensile tests of unnotched specimens and sustained-load tests using notched specimens. Recovery, as indicated by the restoration of original ductility in a tensile test, was attained at baking times of 4 hours or less when the plate thickness ranged for 0.5 mil to 1.25 mils, but recovery was not attained for commercial thicknesses of 2.5 mils or more. Under sustained loading, however, hydrogen-stress cracking occurred in spite of the baking treatment when the plating thickness exceeded 0.5 mil. These results again show that recovery of original ductiliy is not a satisfactory criterion for establishing freedom from embrittlement.

In contrast to the results obtained with conventional cadmium-electroplated specimens, cadmium-titanium electroplated parts have been reported to show increased recovery with increasing plate thickness.(31) This behavior is attributed to the "scavanger effect" of the titanium in the electroplate, and the increased plate thickness merely provides additional titanium for this purpose.

As pointed out previously, cadmium-plating baths without brighteners produce plates of greater porosity than do similar baths that contain brighteners; such porous plates facilitate the removal of hydrogen during baking treatments. The work of Geyer and associates(20) showed that some specimens of AISI 4340 steel (290-ksi strength level) plated from fluoborate cadmium baths with various additions to improve the quality of the plate failed during sustained-load tests after having been baked at 375 F for 23 hours. Also, specimens plated in a high-efficiency cyanide-cadmium bath without a brightener did not fail in the sustained-load test after being baked for 23 hours at 375 F, but when a brightener was added to improve the quality of the deposit, a plated-and-baked specimen failed after only 33 hours under sustained load. This behavior was attributed to the electroplate's being denser and, hence, providing a barrier to hydrogen removal during baking.

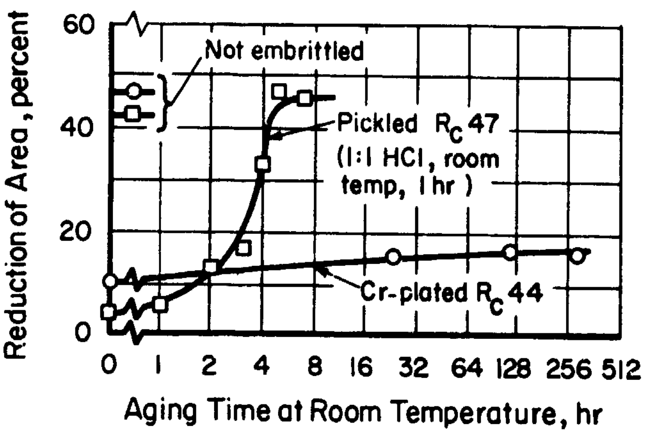


FIGURE 9. EFFECT OF AGING ON THE HYDROGEN EMBRITTLEMENT OF PICKLED AND CHROMIUM-PLATED TENSION SPECIMENS OF 4340 STEEL(45)

Data by North American Aviation
Diameter of specimens = 0.505 in.

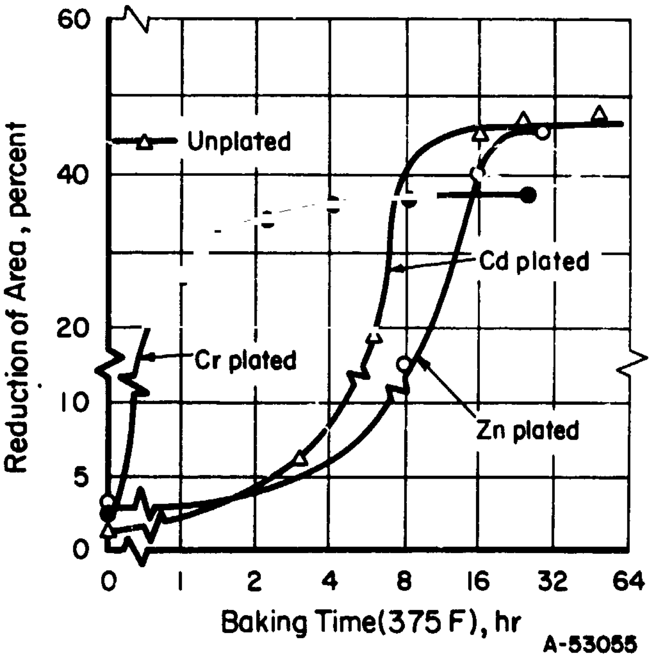


FIGURE 10. EFFECT OF BAKING TIME ON HYDROGEN EMBRITTLEMENT OF CHROMIUM-, CADMIUM-, AND ZINC-PLATED SPECIMENS(45)

Data by North American Aviation
4340 Steel; Hardness = Rockwell C 45.

The recovery of embrittlement in specimens or parts with chromium electroplates is an excellent example of the effect of plate porosity. Even though high-strength steels have been shown to be more severely embrittled by chromium plating than by conventional cadmium plating(23,24,41,42), embrittlement relief is more easily achieved from chromium-plated parts during baking treatments, presumably because the chromium plate is more porous (microcracked). This was effectively demonstrated by Krieg(43) as described previously. Investigators at Convair Fort Worth(44) found that a 23-hour bake at 375 F was not sufficient to relieve embrittlement from specimens with a crack-free chromium electroplate; however, this treatment was effective in eliminating embrittlement from specimens electroplated in a conventional chromium-electroplating bath.

Probert and Rollinson(41) also showed that the barrier effect of chromium plates that ranged in thickness from 0. 25 mil to 0. 50 mil was of a lower order than that for either copper or cadmium deposits of comparable thickness. Complete relief of embrittlement of chromium-plated parts was obtained in less than 5 hours at 100 C (212 F). The lower barrier effect of chromium to the removal of hydrogen during relief treatments was considered to result from the grain size and the natural crack pattern of deposits in the high-hardness range. It was found that, on increasing the thickness of chromium above 0. 5 mil to effect satisfactory relief from embrittlement, it was necessary to exceed the time-temperature conditions established for copper and cadmium deposits. The results of their studies are shown in Figure 11.

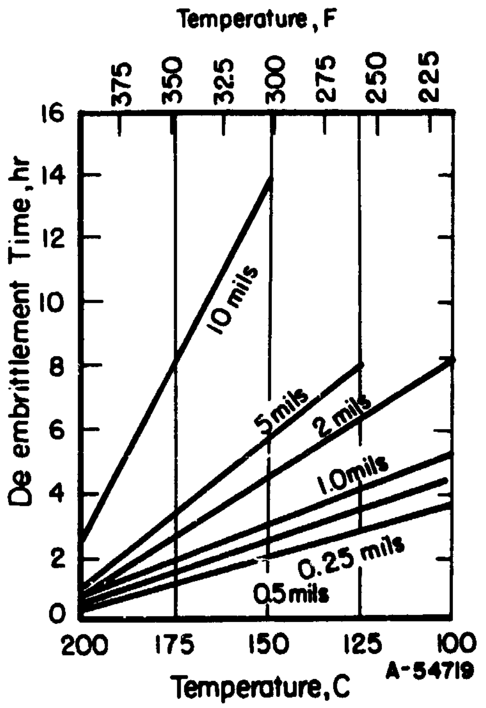


FIGURE 11. HYDROGEN-EMBRITTLEMENT RECOVERY TIMES AND TEMPERATURES FOR DIFFERENT THICKNESSES OF ELECTRODEPOSITED CHROMIUM (STANDARD BATH)(41)

The strength level of an electroplated part also influences the effectiveness of embrittlement-relief treatments. As was shown in the section on electroplating, lost ductility generally can be recovered in steels with lower strength levels by short baking times at a given temperature, but ductility may not be completely recovered in higher strength steels after considerably longer baking times at the same temperature. This behavior seems to be closely related to the susceptibility of the material to embrittlement; that is, recovery is more easily achieved in the less susceptible materials. This effect is shown by the plating processes used by one manufacturer for cadmium coating high-strength-steel fasteners, as shown in Table 10.(48)

TABLE 10. CADMIUM-COATING PROCESSES USED ON HIGH-STRENGTH-STEEL AIRCRAFT FASTENERS(48)

Tensile Strength of Fastener	Less than 180,000 psi	180,000 to 250,000 psi	250,000 psi and higher
Specification	QQ-P-416	NAS 672	MIL-C-8837
Plating Procedure	Cyanide	Fluoborate	Vacuum
Baking Practice	3 hr at 375 F	23 hr at 375 F	None

In selecting a baking treatment, several factors must be considered. First, the time and temperatures selected cannot cause a degradation of the properties of the base steel. Consequently, selected temperatures are usually at least 50 degrees below the tempering temperature of the base steel. Also, the temperature selected must not cause damage to the plate. For example, temperatures over 400 F can cause discoloration of cadmium electroplates. Also, temperatures above 610 F, the melting point of cadmium, must be avoided because liquid cadmium can cause embrittlement of steel. Under many conditions, cadmium embrittlement of steel can occur at temperatures appreciably below the melting point of pure cadmium, and failures have been observed at 500 F.

In the case of age-hardening steels electroplated with chromium and nickel, the latitude in selecting baking treatments would appear to be much wider, as these materials are usually hardened by aging reactions taking place at considerably higher temperatures than the tempering temperatures applied to ultrahigh-strength steels, and these plates are not so severely affected by higher temperatures as is cadmium. For example, some investigators have used temperatures up to 1000 F to bake out chromium-plated AISI Type H-11 steel, and temperatures up to 600 F have been used to bake out nickel-chromium-plated specimens of 18Ni maraging steel.

The results of various investigations on the effectiveness of various hydrogen-embrittlement relief treatments indicate that many variables influence the selection and effectiveness of these treatments. These variables include steel composition, strength level, applied-stress level, test method, the presence of a coating, and the type, structure, and thickness of the coating.

The results show that hydrogen is more easily removed when no coating is present. When the section size is not too great, baking at 375 for 1 to 5 hours appears to restore the properties of high-strength steels that have been pickled or cathodically charged. However, when a coating is present, longer baking times are necessary. Thin electroplates and porous electroplates facilitate hydrogen removal, while thicker plates and dense plates hinder hydrogen removal during baking treatments. Also, steels of lower strength level (below about 180 ksi) have been shown to be nearly completely relieved of the effects of hydrogen by baking treatments. However, the higher strength steels have shown a propensity toward hydrogen-stress cracking even after longer baking treatments.

Investigators have shown that the ductility of a steel part, as measured in a conventional tensile test, may be completely restored by a baking treatment, but the steel may still be susceptible to hydrogen-stress cracking under sustained tensile stresses. Therefore, only when the variables are fixed can a relief process be said to be effective, and only for those fixed conditions.

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