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ELECTROLESS NICKEL AS A REPLACEMENT FOR HARD CHROMIUM
THE PHOSPHORUS CONTENT MAKES THE DIFFERENCE

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Introduction

Electroless nickel technology has been available to engineers for over 30 years. Electroless (or autocatalytic) nickel deposition, like hard chromium plating, is applied for the engineering properties obtained from these respective deposits. A wide variety of electroless nickel process types are available to choose from with the more common being alloys of phosphorus or boron. The properties of the electroless nickel deposit vary markedly with deposit composition and the plating conditions. For this reason, care must be taken in matching a particular deposit with the application.

Electroless nickel deposition has been periodically examined as a possible replacement for hard chromium plating because of the advantages offered by these deposits including: uniform plate thickness distribution, good corrosion and wear resistance, and deposit hardness (1,2,3). Unfortunately, the use of electroless nickel as a replacement for hard chromium has not flourished. It has likely experienced limited growth in this market area as a result of previous failure and the misconception that electroless nickel is more costly to produce than hard chromium. This failure was likely a result of the improper understanding of electroless nickel's properties, and the types of processes available to obtain the desired characteristics. The cost issue may vary somewhat with application, but an excellent cost comparison has been provided recently by Jeanmenne (3). This report considered the performance of the deposits as well as costs involved with racking (thieving & fixturing), masking, post grinding, process chemistry, and waste treatment.

Throughout the years of electroless nickel's development, engineers who have attempted to replace hard chromium deposits may have also discovered that many of the reported electroless nickel properties were not reproducible. This made replacing hard chromium with electroless nickel that much more difficult. In the past electroless nickel was often treated as a generic coating. Close examination of deposit properties such as microhardness, wear resistance and internal stress have highlighted differences within each type and formulation.

Current restrictions on chromium waste discharge and the recent development of the lower nickel phosphorus technology allows a more direct comparison to hard chromium deposits to be made. The purpose of this paper is to bring some of the data on the range of electroless nickel deposits to provide a comparison with the properties of hard chromium. In addition, the data will demonstrate that the phosphorus content does make a difference.

Hard Chromium Deposition

The baths used to deposit hard chromium have been described by Dubpernell (4), and Guffie (5). Many processes operate at 32 oz/gal of chromic acid with a ratio of chromic acid to sulfate at about 100:1 and a temperature range of 130-150°F. The current density range is usually 1-3 amps per square inch. Several high speed catalyst formulations are available which produce deposits with somewhat different properties.

Electroless Nickel Deposition

With a variety of electroless nickel processes available containing from less than 1% phosphorus to more than 13% phosphorus, choosing the process that will produce the optimum phosphorus content for a given application is difficult because of the effects the phosphorus content has on the properties of the Ni-P alloy. Trying to answer the question "What is the optimum phosphorus content required for my application?" can be a difficult decision.

In general, higher phosphorus alloy deposits are softer as plated, can be heat treated to improve hardness, are non-magnetic as plated, and they do not wear quite as well but are more corrosion resistant especially in acid environments. Conversely, the lower phosphorus alloy deposits tend to be harder both as plated and after heat treatment. The lower phosphorus alloy deposits wear better and tend to exhibit better corrosion resistance in alkaline environments.

Experimental Considerations

The electroless nickel deposits were prepared using the commercial processes and following the procedures provided by the commercial literature.

ASTM microhardness specifications E 384 and B 578 and ISO 4516 covering Knoop and Vickers microhardness testing were followed. The microhardness values obtained using the Knoop and Vickers indenters are different due the the different indenter shapes, and the results cannot be used interchangeably. Comparisons between Knoop, Vickers and Rockwell C can be obtained if measurements are made using comparable standards. Figure 1 shows the relationship between Knoop and Vickers values and Figure 2 shows the relationship between Knoop and Rockwell C obtained using steel Rockwell C standard blocks. It is also important that the load be specified since the microhardness values change with load (6). Microhardness was measured using a Shimadzu Type M Hardness tester with a Knoop indenter at a 100 gram load.

Wear is often measured as weight loss of material during use. There is no shortage of studies on the wear properties of electroless nickel deposits, a few of which are referenced here (1,7-13), and most of them use hard chromium as a comparison. Many of these studies consider the effect of hardness on the wear properties obtained. Not all studies show a direct relationship of hardness to wear resistance because of the various types of wear and their conditions.

The wear characteristics of the various electroless nickel deposits were recently investigated by Weisenberger and Greene (14). This work emphasized the Tabor Abrasive wear resistance (TWI- Tabor wear index) and Falex Adhesive wear resistance of a wide range of Electroless boron and phosphorus deposits. These tests have been used frequently to evaluate coatings for wear resistance although the conditions of the testing often vary markedly.

The Teledyne Taber Abraser is described in the ASTM C 501 specification. Following earlier work (1,8), the plated panels were tested using CS-10 abrasive wheels that were refaced for 50 cycles over 150 abrasive paper after each 1000 cycles. The initial 1000 cycle results were discarded, as is general practice. The weight loss of samples was recorded after each 1000 cycles.

The adhesive wear tests were accomplished using the Falex Wear tester which is described in ASTM D 2670. The plated 6.35 mm (0.25 in) diameter pin (SAE 3135) is rotated at 290 rpm between two unplated (AISI 1137) V-blocks under load. The procedure used by Weisenberger and Greene (14) and Parker (1) was reproduced: 1) 5 minute break-in at 50 lb load; 2) 60 minutes at 200 lb load; 3) 40 minutes at 400 lb load. A white mineral oil (340-365 SUS) was used as a lubricant in these tests. In order to improve adhesion on the hardened Falex pins, a sulfamate nickel strike was plated over the pins before they were plated in the electroless nickel plating bath.

Plated deposits are deposited with some form of internal stress (either tensile or compressive). Deposits with tensile stress shrink and compressive deposits expand to relieve the stresses. As the tensile stress increases, there is a greater loss in fatigue strength. Compressively stressed deposits have the least loss in fatigue strength and, in those applications where fatigue strength is especially important, the use of electroless nickel has proven effective (15). The cracking associated with hard chromium deposits is due to high tensile internal stresses (16).

ASTM B 636 describes the use of the spiral contactometer to measure stress of electroplated deposits. A few procedure modifications are required to adapt its use to electroless nickel plating. Much of the older published data on electroless nickel stress can be questionable because of problems in stress measurement. The stress values vary significantly with the techniques, apparatus, and the thickness of the deposit. Figure 3 illustrates the variation of internal stress with deposit thickness. In addition, the internal stress measured at plating temperature is considerably different than that obtained when the helix is cooled to room temperature.

Comparison of Properties

Microhardness

There is no shortage of data on the hardness/microhardness of chromium deposits in the literature (17-20). The microhardness of the chromium deposit has been shown to vary with the plating conditions. The variation of the microhardness with operating temperature and current density is shown in a topological format in Figure 4. The data reproduced here was obtained for a chromic acid sulfate bath. The fluoride catalyzed process produces a similar map (19). The most common plating conditions are about 140°F and 1-3 amps per square inch (144-432 ASF) suggesting a hardness range of 950-1100 HV. A recent paper (17) reported conventional deposits with a microhardness range of 800-1000 HK_{100} and mixed catalyst deposits at 950-1050 HK_{100} confirming the original observations in Figure 4. Hard chromium deposits also soften with subsequent heat treatments.

The microhardness of electroless nickel alloys is affected by the alloy composition and subsequent heat treatment temperatures. Table 1 illustrates the typical as plated microhardness ranges and heat treatment characteristics of representative phosphorus and boron alloys (14). The hardest as plated deposits are the 2.0% boron with a range of 770-809 HK_{100}, and the 4% phosphorus (alkaline and acid baths) at a range of 688-802 HK_{100}. Post plating heat treatments increase the microhardness in both types of deposits. Figure 5 shows the relationship between heat treatment temperature and the resulting microhardness depending on the amount of phosphorus in the deposit. Figure 6 shows the same relationship for boron electroless nickels. The heat treatment conditions to obtain the best hardness can vary with the deposit, and the conventional 400°C for one hour is not always the best treatment (20).

The difficulties in comparing microhardness values expressed as various units has been recently discussed (6). The Knoop, Vickers and Rockwell C values cannot easily be converted. The best method of obtaining correct values is to use the three indenters on the same metal and with the same load. Figures 1 and 2 were obtained by using

Rockwell C standard steel hardness blocks with the Knoop and Vickers indenters.

Wear Characteristics

Taber abrasion wear results using the 3-4% phosphorus deposit are shown in Figure 7. A summary of abrasion wear results for the full range of electroless nickel deposits (14) is provided in Figure 8 and Table 2. Hard chromium provides the best result with this test with a Taber Wear Index (TWI) of 3-4 mg/1000 cycles. The 4% phosphorus deposited from the acid and alkaline baths and the 0.2% boron alloys provide the next best results with a TWI of 8-10 for both as plated and heat treated deposits. It is interesting to note that the 0.2% boron deposit did not have a high microhardness as plated or after subsequent heat treatment as compared to the 2.0% boron deposit but provided the best abrasive wear. The other deposits are shown to wear poorly in the as plated condition but improve when heat treated.

The Falex Wear Tester may be used to test adhesive wear in many ways, since there are standard methods. Parker (1) tested all possible combinations: plated pin and blocks, plated pin and unplated blocks, and unplated pin and plated blocks. Weisenberger and Greene (14) chose to work with the plated pin and unplated blocks since some of the more important electroless nickel applications involve a plated pin assembled with unplated gears (something that might be found in a automobile transaxle assembly). The load conditions chosen were those used by Parker (1).

Figure 9 displays the results obtained using the Falex tester with pins plated with 4% phosphorus deposit against the unplated blocks under two load conditions. These results can be compared with similar figures plotted for the other electroless nickel deposits (14). Figure 10 compares the Falex results for the range of deposits heated to their optimum (maximum) microhardness. The chromium plated pin survives with the least amount of loss, but the mated surface is badly damaged. It is known that galling occurs when both pins and blocks are coated with hard chromium (1). Others have also shown that chromium deposits do not provide the best wear under certain conditions. Jones (17) recently reported subjecting hard chromium deposits to higher loads for longer times and saw considerably higher wear. All of the electroless nickel deposits, being somewhat lubricous, are much more forgiving, and damage to the mated surface is significantly reduced. Of these, the 4% and 9% phosphorus alloys (acid baths) provided the best wear resistance to the plated surface and also provided the best protection for the mated blocks.

Blau (21) points out that a persistent problem in engineering wear testing procedures involves the correlation of lab bench testing to actual wear behavior in the field. In many field wear situations, the precise loads, temperatures, contact geometries and chemical environments are difficult to know. It is also likely that more than one mode of wear may be operating and the contact conditions could change with time. The test results presented in this and earlier papers provide definite indications of the characteristics of the plated deposits. However, the ultimate test is the use of the deposit in the specific application.

Internal Stress

The internal stress of hard chromium deposits is highly tensile. Figure 11 shows the internal stress measured for deposits from a sulfate bath by Stareck (22). The stress is very high for deposit thicknesses less than 1 mil. The stress drops with increasing thickness as the deposit begins to form microcracks. Some stress relief may also be accomplished as chromium deposits form inside the cracks to provide some expansion forces (22).

Past studies have shown the internal stress of electroless nickel deposits to increase with plating bath age, possibly the effects of sulfate or phosphite build up in the solution. This increase in the stress can have a negative effect on the fatigue life of high strength alloy substrates used in the aircraft/aerospace industry.

It has been shown that the internal stress of high phosphorus deposits tend to be compressive for a few metal turnovers then become highly tensile. The 4% phosphorus deposits exhibit low internal stress which can be slightly compressive or slightly tensile depending on conditions of deposition (see Figure 3). At low thicknesses, the stress is compressive, and as the deposit thickness is increased to 0.9 mil, the stress is near zero and increases to a very low tensile stress as deposit thickness continues to increase.

Summary

The wear, stress and hardness characteristics of electroless nickel deposits are strongly affected by the alloy content and conditions of plating.

The lower phosphorus electroless nickel processes (in the range 3-4% P) appear to be filling a long needed requirement in the plating industry. The high as plated and heat treatable microhardness, very low tensile or compressive stress and good wear characteristics make it ideally suited to replace hard chromium in many applications.

The wear resistance properties and uniform deposition thickness of electroless nickel alloys have always been one of the key features for this type of deposit. The lower electroless nickel phosphorus deposits in the range of 3-4% have the best properties to perform under the varying conditions stated.

The 3-4% phosphorus deposits exhibit as plated hardness that is similar to that of the much more expensive boron alloy deposits and can be heat treated to match the hardness of hard chromium.

While hard chromium performs well against a hard abrasive surface like the Taber CS-10 wheel, it is not so attractive when it must be mated with other softer metal surfaces. Since many wear situations can generate heat, low phosphorus electroless nickel deposits are preferable over hard chromium deposits because electroless nickel microhardness increases with increasing temperatures while hard chromium deposits soften under those conditions.

The 3-4% phosphorus and high phosphorus deposits provide near zero to low compressive stress which provides for the least loss in fatigue strength.

The lower phosphorus process and deposits have much to attract the parts designers as well as the platers.

Acknowledgments

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Table I
Microhardness for Electroless Nickel Deposits
Heated at Temperature for One Hour
HK_{100} Microhardness

Deposit	As Plated	250°C	300°C	350°C	400°C	450°C
Chromium	800-1000	Deposits soften with increasing Temps.				
Alkaline 4%P	688-709	814-870	856-906	855-942	794-895	630-744
Acid 4% P	728-802	782-838	795-877	980-985	927-987	854-860
Acid 9% P	513-527	612-643	872-918	862-952	834-897	800-934
Acid 11% P	517-531	560-572	870-918	856-977	866-967	811-894
0.2% B	575-603	598-658	593-630	525-540	507-533	439-514
2.0% B	770-809	1127-1186	1041-1180	975-1037	926-960	809-994

Table II
Taber Abrasive Wear Results
CS-10 Wheel at 1000 gram load

Deposit	Taber Wear Index			
	As Plated	Best Hardness	Treatment	Ref
Chromium	3			1
EN-Kanigen	18	8	290°C 10hr	1
Acid 8.5%P	28	11	400°C	11
Acid 12%P	30	12	400°C	11
Alkaline 4%P	9	8	300°C	14
Acid 4%P Fresh	9	7	360°C	
Acid 4%P 8 T.O.	9			
Acid 9%P	20	10	350°C	14
Acid 11%P	24	10	400°C	14
0.2% B	8	8	350°C	14
2.0% B	23	13	350°C	14

Figure 1
Microhardness Units Comparison
Vickers Vs Knoop

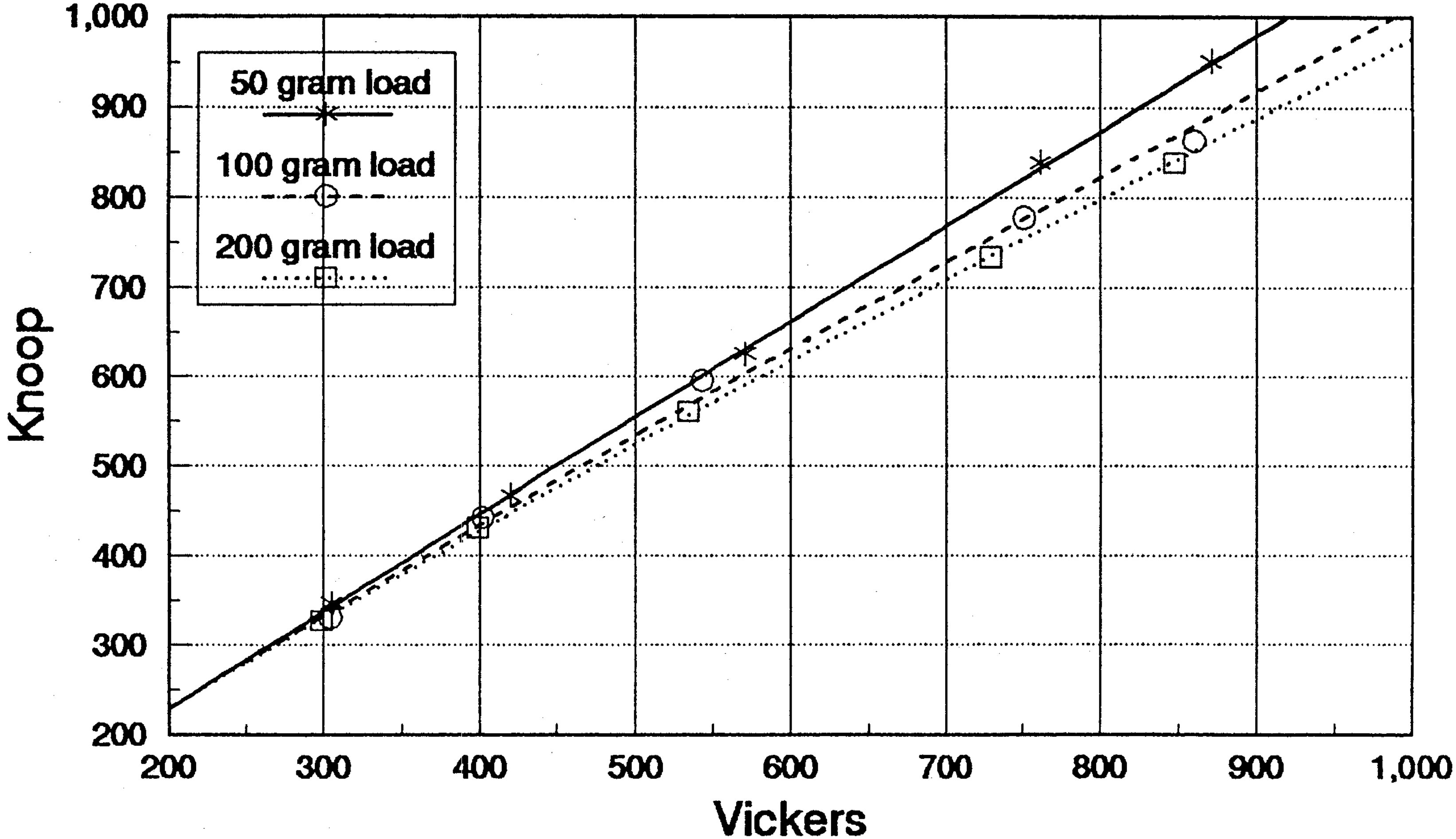


Figure 2
Microhardness Units Comparison
Knoop Vs Rockwell

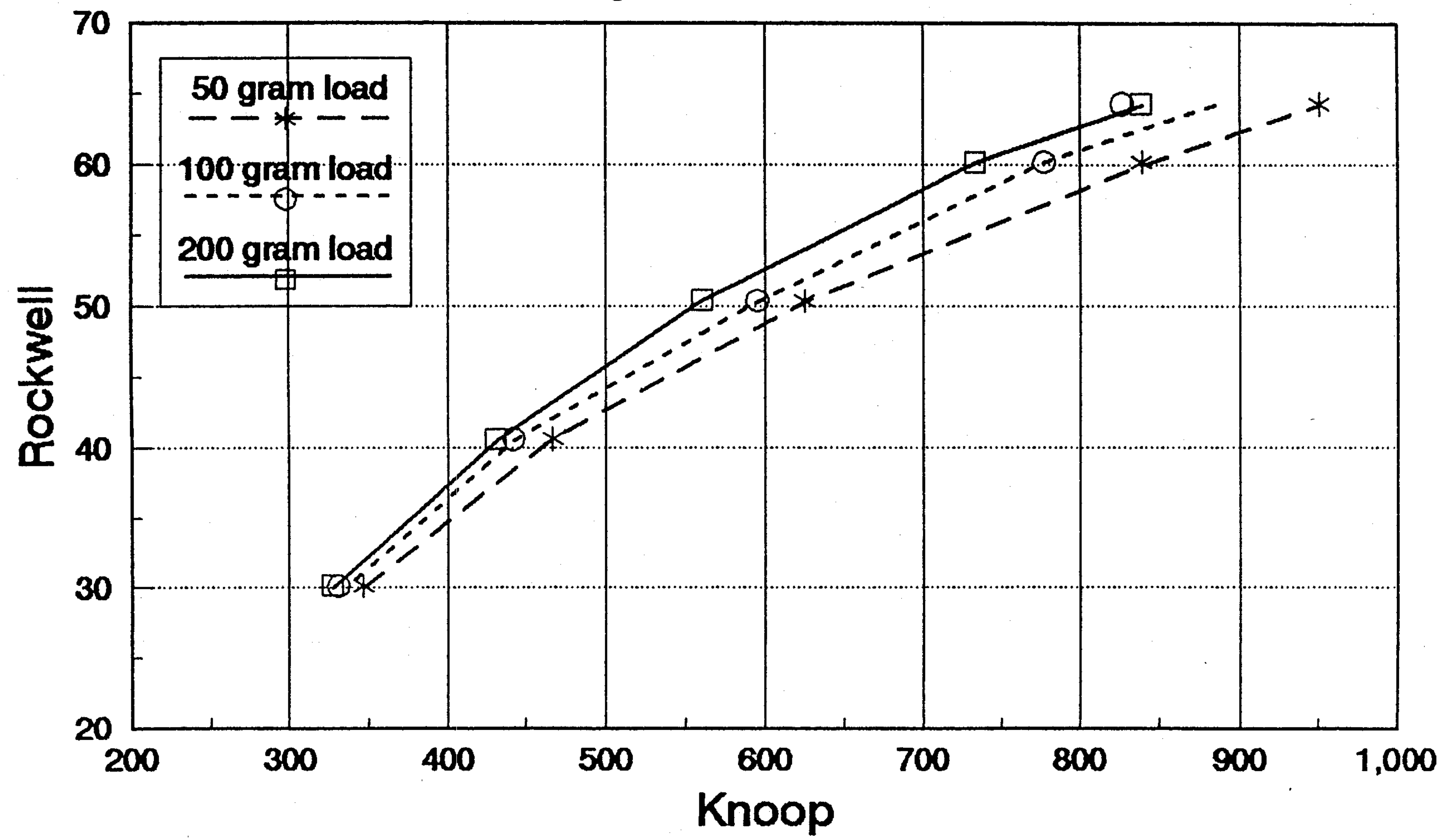


Figure 3
3-4% Phosphorus Deposit
Internal Stress Vs. Thickness

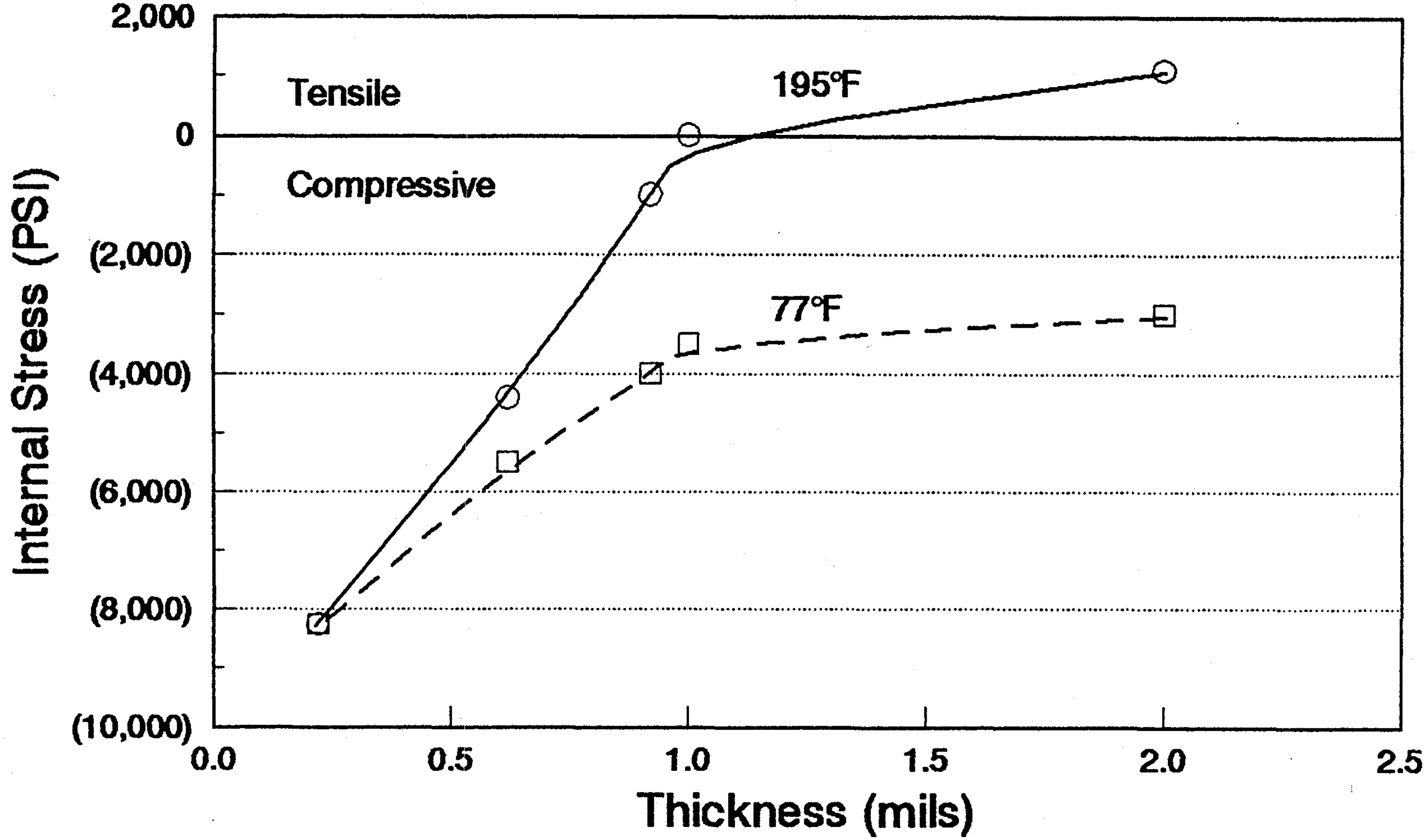


Figure 4
Electrodeposited Chromium
Hardness vs Conditions

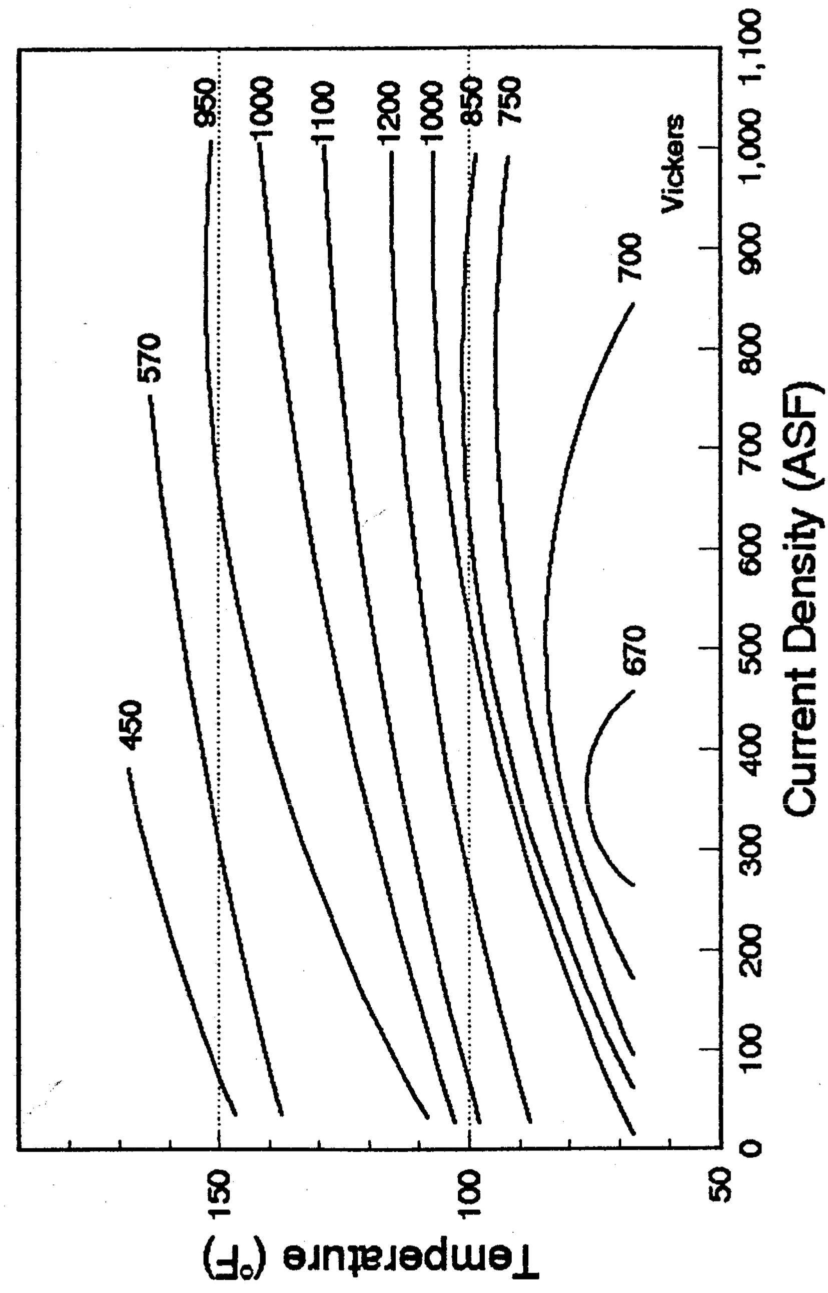


Figure 5
EN Microhardness vs. Heat Treatment

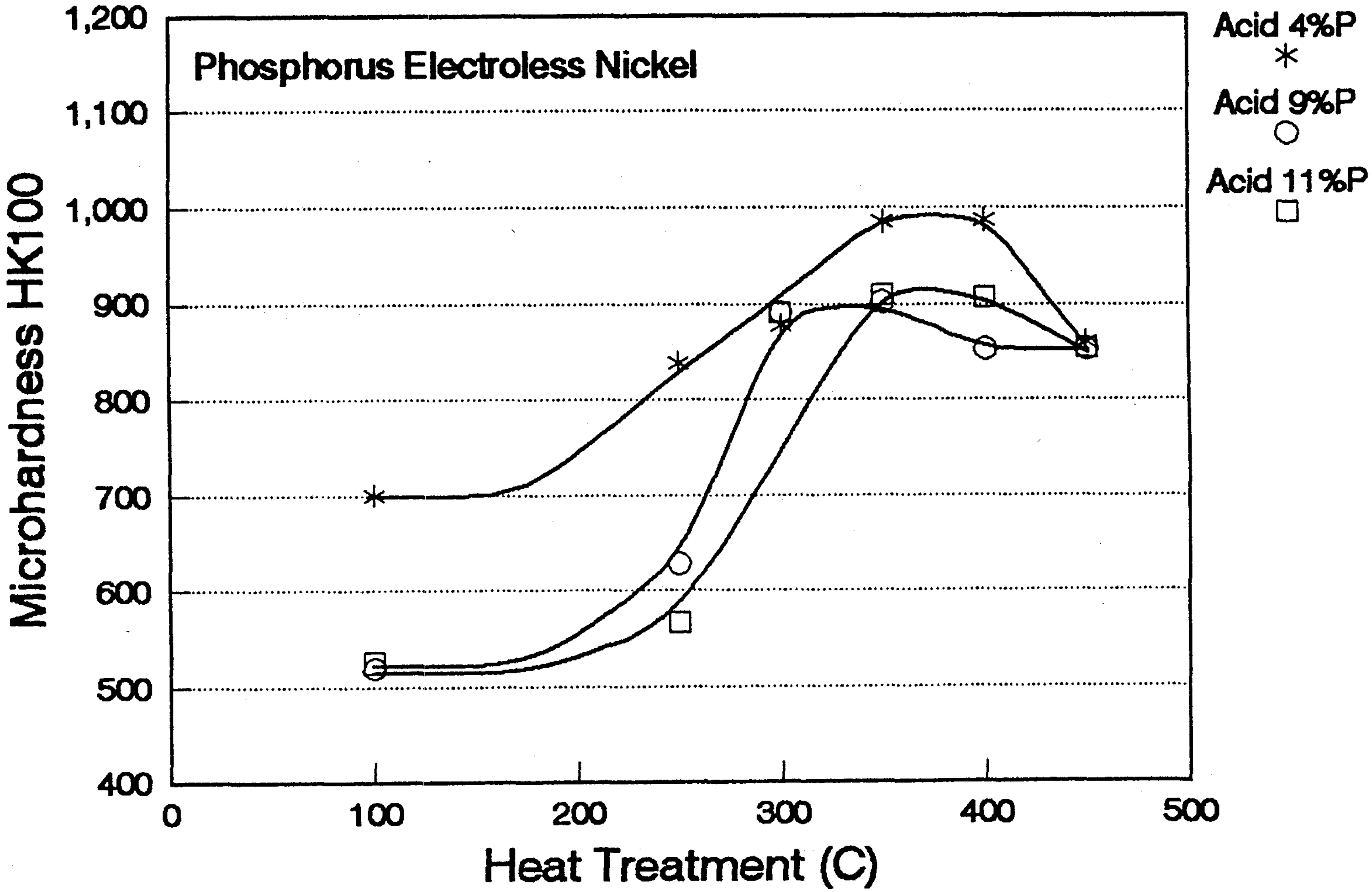


Figure 6
EN Microhardness vs. Heat Treatment

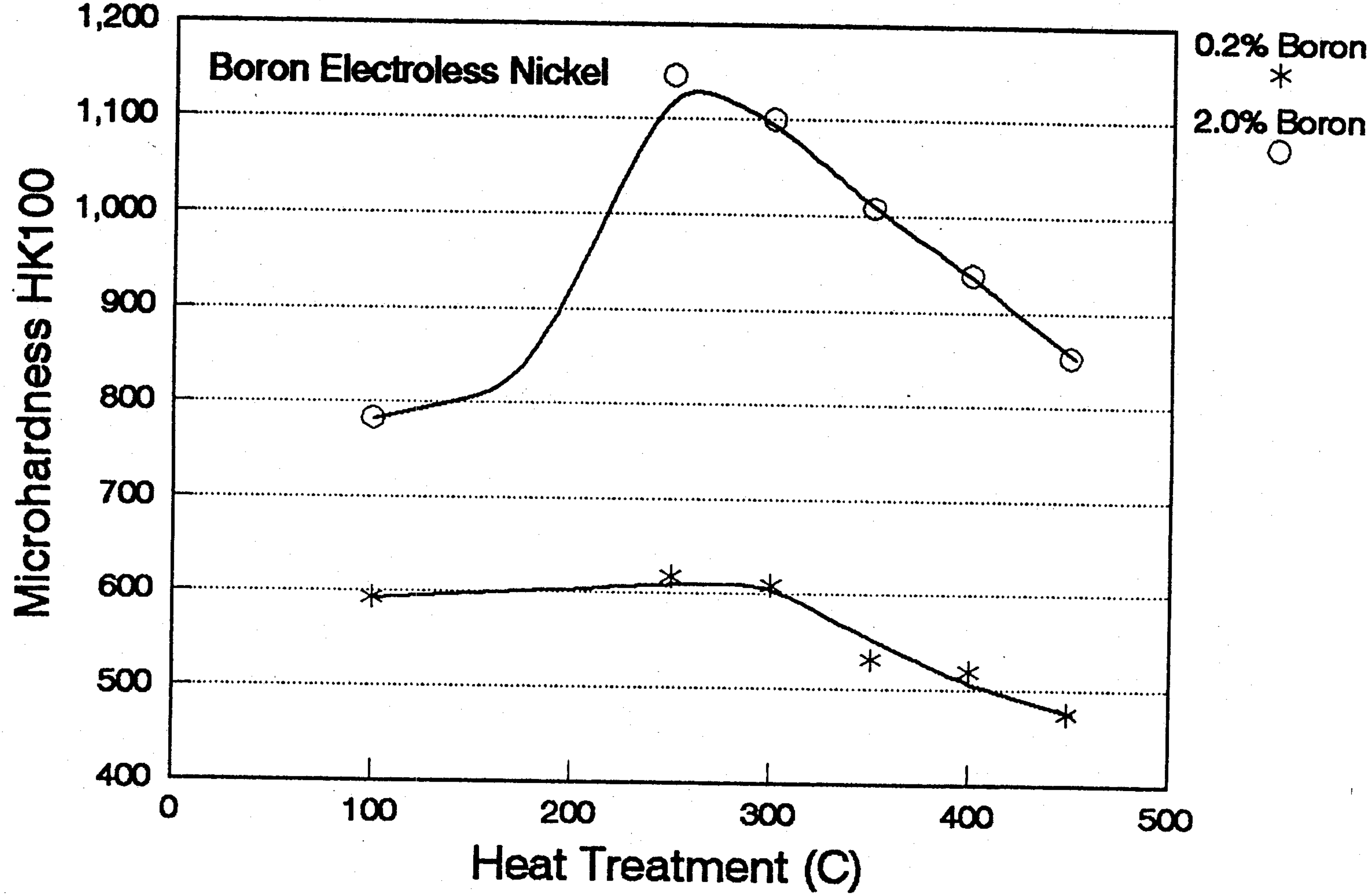


Figure 7
Taber Wear Index for 3-4% Phosphorus Deposit

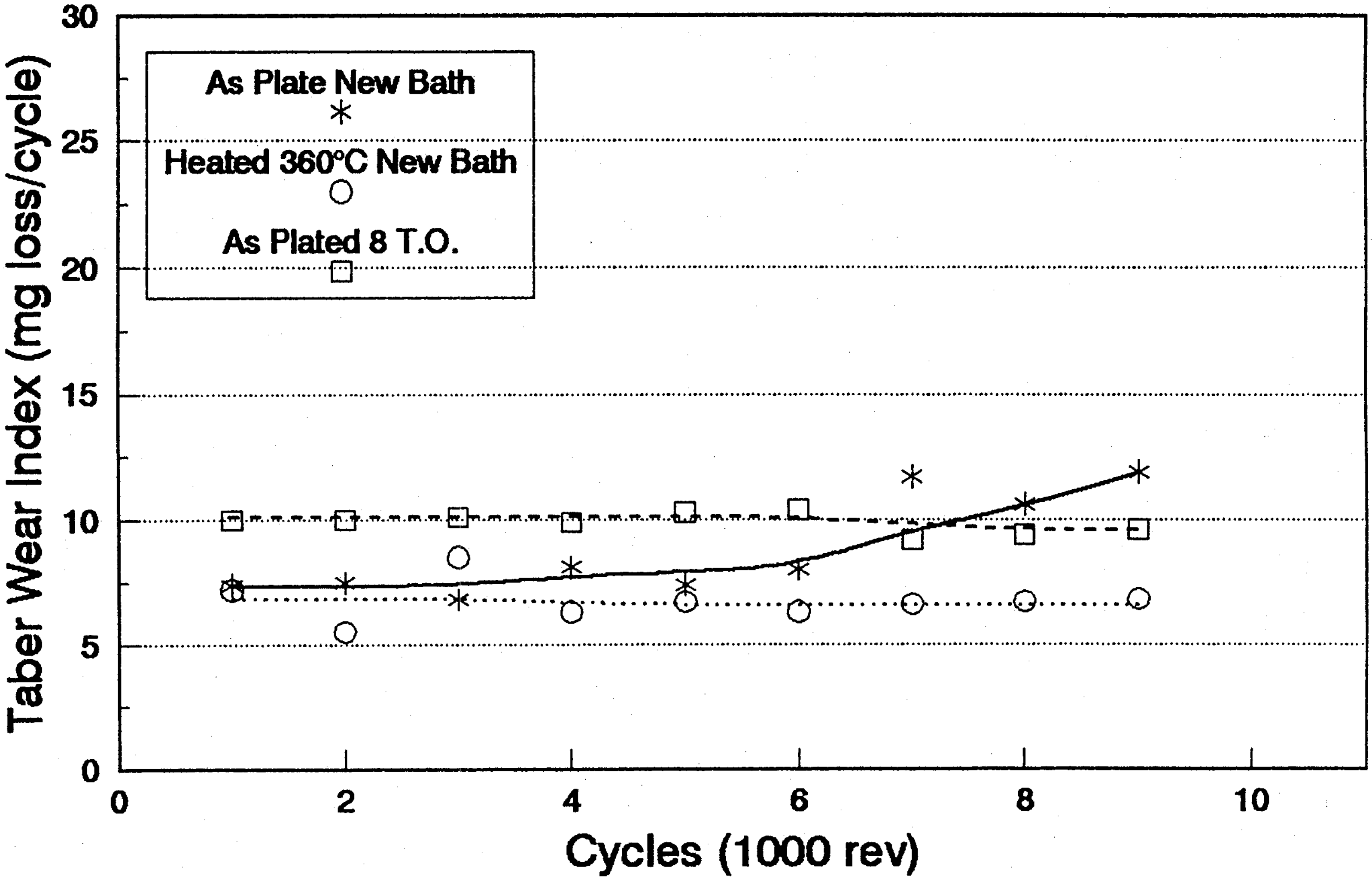


Figure 8
Taber Abraser Wear

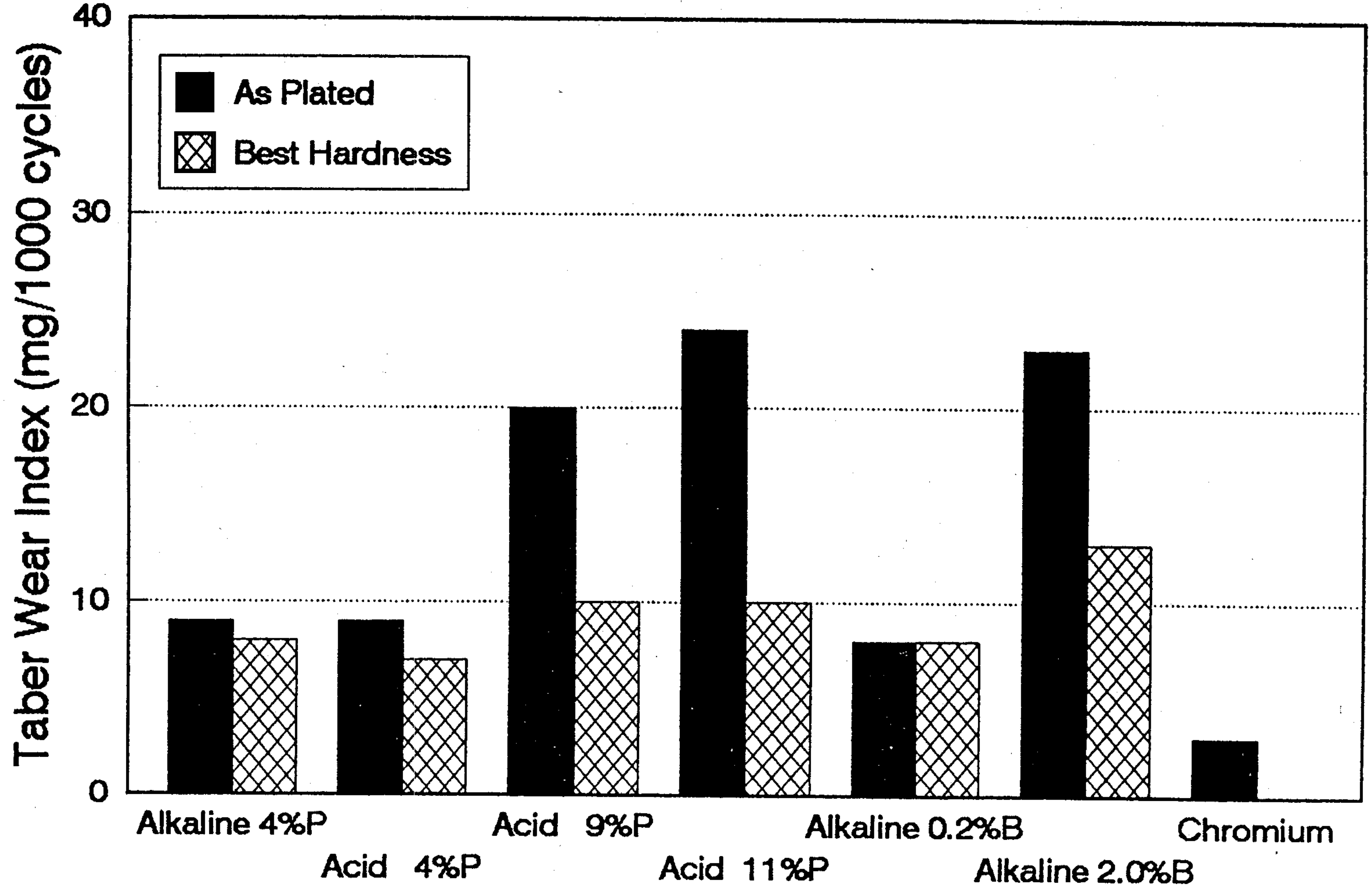


Figure 9
Falex Wear: Plated Pins vs. Unplated Blocks
4% Phosphorus Deposit

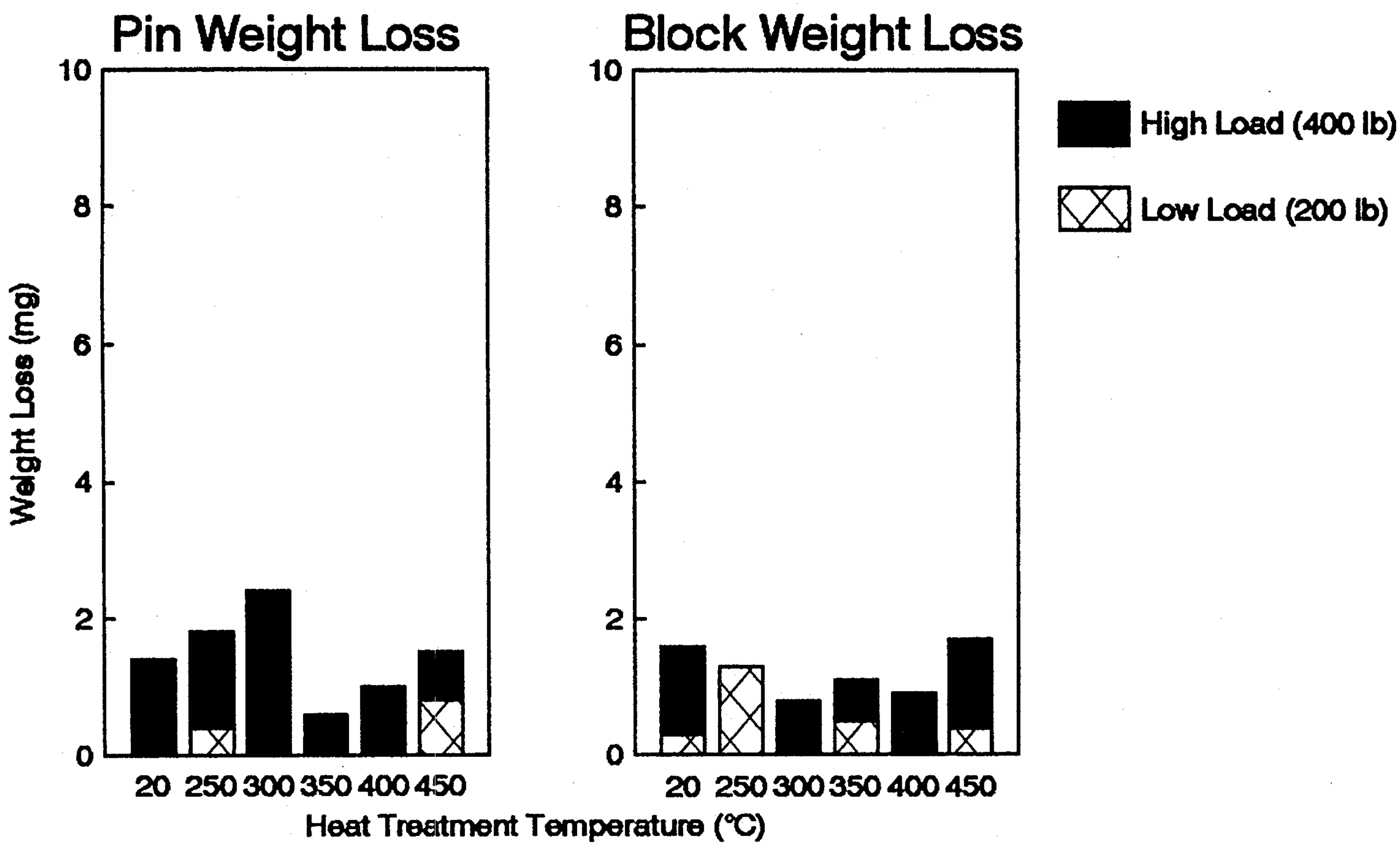


Figure 10
Falex Wear Plated Pins vs. Unplated Blocks

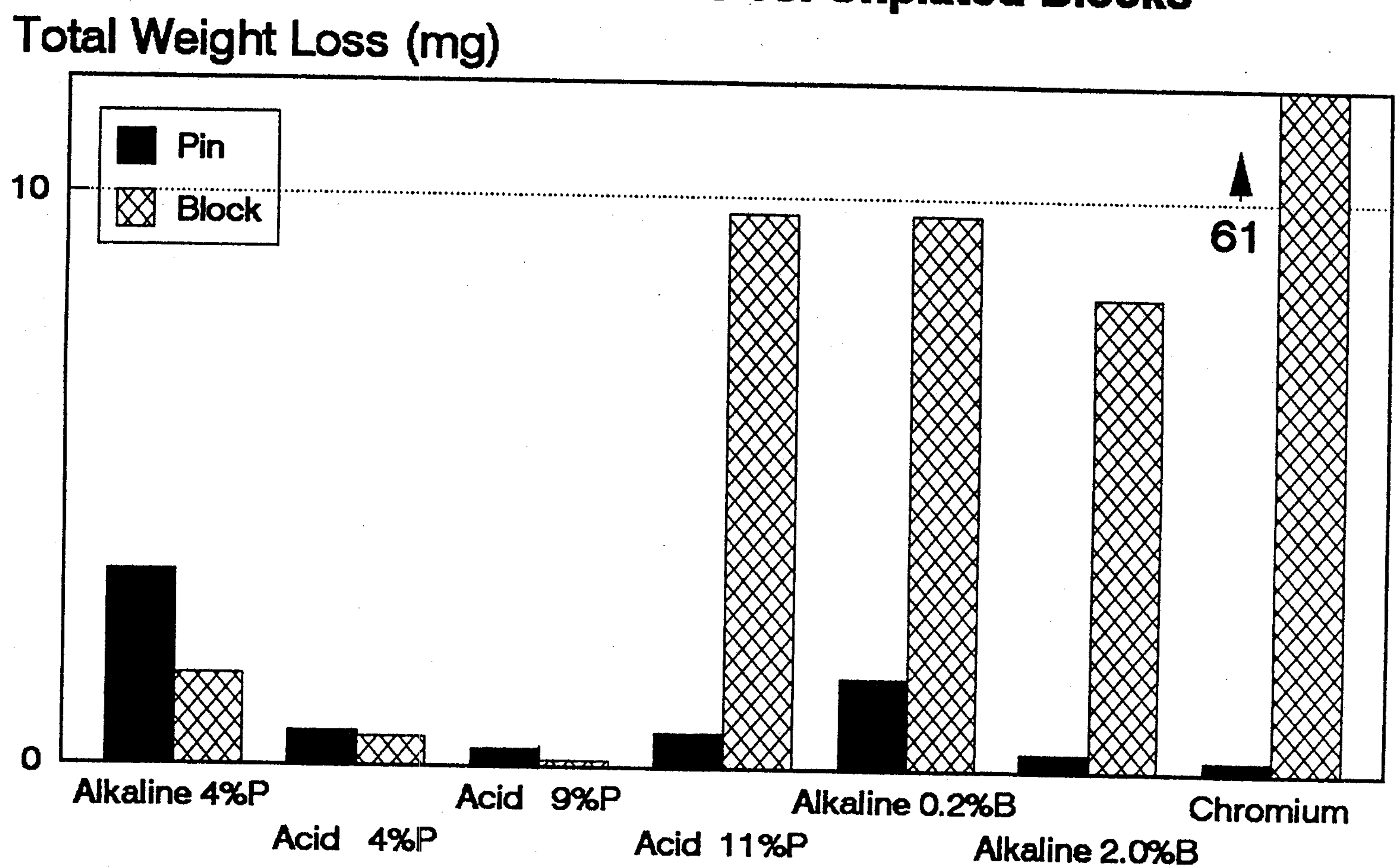
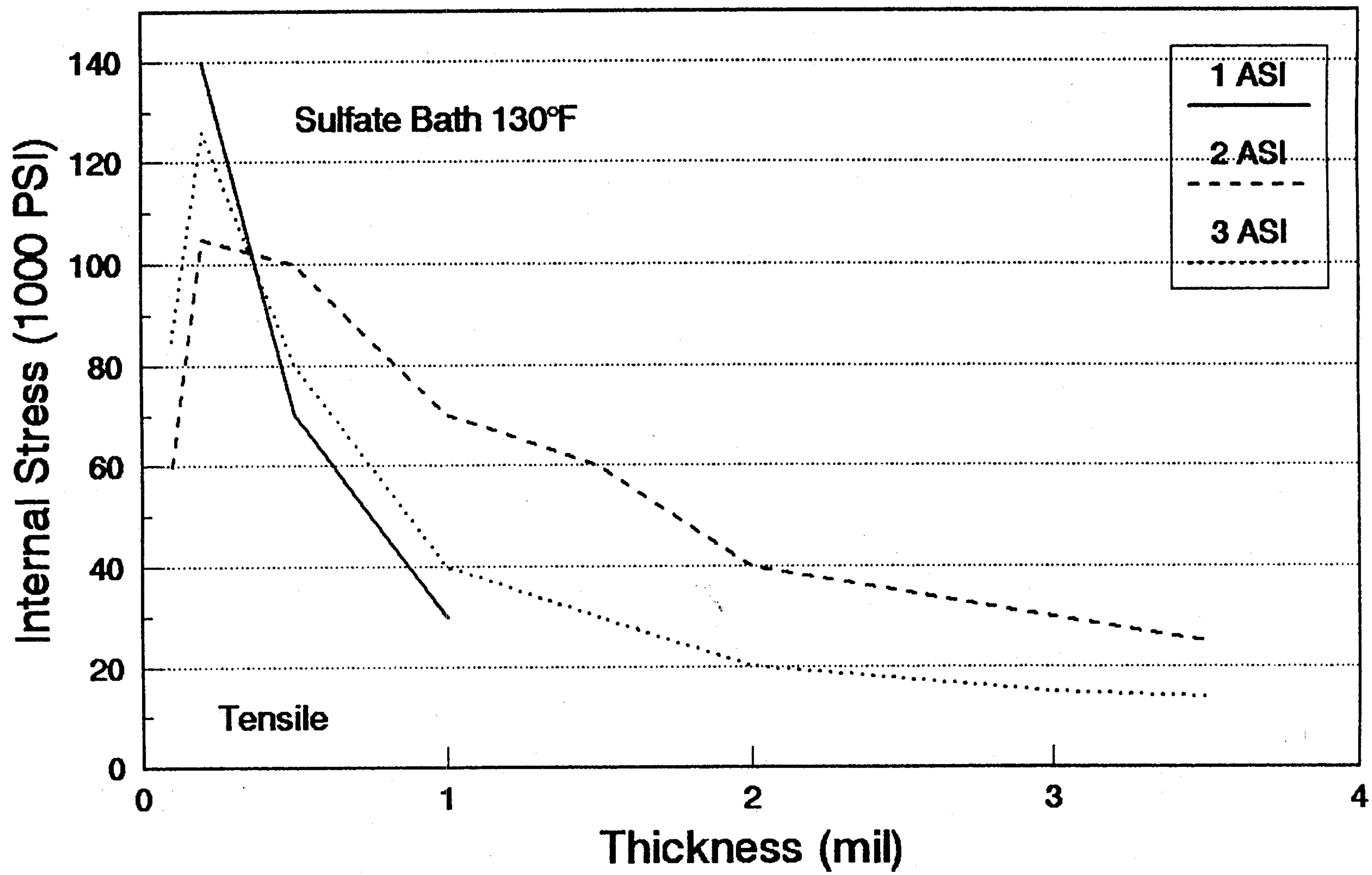


Figure 11

Hard Chromium Stress Vs. Thickness



July 25, 1992

Mr. J. Howard Schumaker, Jr.
Executive Director
American Electroplaters and Surface Finishers Society
12644 Research Parkway
Orlando, FL 32826-3298

Mr. J. Howard Schumaker Jr.

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respectfully

Vic Young
Staff Engineer
Waste Reduction Resource Center

American Electroplaters and Surface Finishers Society

August 4, 1992

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ELECTROLESS NICKEL AS A REPLACEMENT FOR HARD CHROMIUM
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Abstract

The wear resistance properties of electroless nickel alloys have always been one of the key design features for this type of deposit. However, in the past, when a parts designer needed a very hard, wear resistant surface there were few choices, with hard chrome or boron electroless nickel being the main alternatives. Unfortunately, hard chrome does not provide a uniform thickness and boron electroless nickel is very expensive.

The other types of electroless nickel have been useful in a wide range of applications, but never came close to the wear resistance and hardness required for some applications without heat treatment. The recent development of high speed acidic processes that deposits electroless nickel alloys with 3-4% phosphorus provides an answer to some of these design problems. This type of deposit provides a plated microhardness that equals the as plated hardness of boron electroless nickel, and a heat treated microhardness that is similar to that obtained by hard chrome.

The wear, internal stress, and microhardness characteristics of low phosphorus electroless nickel will be compared with the characteristics of other electroless nickel deposits and hard chromium.