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EFFECTS OF ELECTROLESS NICKEL PROCESS VARIABLES ON QUALITY REQUIREMENTS

FINAL REPORT

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by

Fielding Ogburn

and

Christian E. Johnson

JUNE 1976

U.S. ARMY ARMAMENT COMMAND

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National Bureau of Standards
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GENERAL THOMAS J. RODMAN LABORATORY
ROCK ISLAND ARSENAL
ROCK ISLAND, ILLINOIS 61201

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The project objective was to determine the effects of production procedures on the characteristics of electroless nickel coatings. Deposition rate, phosphorus content, hardness, appearance, and metal distribution are reported for deposits from several hypophosphite type electroless nickel baths, both proprietary and non-proprietary. The baths were operated under a variety of conditions with variations of composition. Extensive data are given on the relation of deposit hardness to phosphorus content and to heat treatment at 100, 200, and 400°C. Some data are given relative to electroless Ni-B, Ni-P-Cu, and Ni-P-Mn alloys.

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FOREWORD

This report was prepared by Mr. Fielding Ogburn and Mr. Christian E. Johnson of the Corrosion and Electrodeposition Section, Metallurgy Division, Institute for Materials Research, National Bureau of Standards, Washington, DC., in compliance with MIPR A1-2-65509-M2-M9. This work was performed for the Research Directorate, General Thomas J. Rodman Laboratory, Rock Island, Illinois, with Mr. Donald H. Sale as Project Engineer.

The work was authorized as part of the Manufacturing Methods and Technology Program of the U. S. Army Materiel Command and was administered by the U. S. Army Production Equipment Agency.

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Objective

The general objective of the project under which this work was done was to determine how characteristics of electroless nickel coatings are influenced by the operating variables of the process. The operating variables were to extend to levels outside the normal operating ranges.

In this report we include deposits from non-proprietary baths and three proprietary baths. Appearance, structure, plating rate, phosphorus content, hardness, heat treatment, and thickness uniformity of the deposits are discussed. The hardness data in conjunction with heat treatment are fairly extensive.

Solutions Used

Many of the electroless nickel (Ni-P) deposits were obtained from a solution similar to those reported by Brenner:[1]

$NiCl_2 \cdot 6H_2O$	30 g/l
Sodium hypophosphite	10 g/l
Sodium hydroxyacetate	50 g/l

As prepared, this solution has a pH of about 6.6; but with use, the pH quickly drops to the buffered range of about 4.0-4.5. Normally the process was operated at or close to 96°C.

A modification of this Brenner bath was used to obtain deposits with less than 4% phosphorus:

$NiCl_2 \cdot 6H_2O$	60 g/l
Sodium hypophosphite	1 g/l
Sodium hydroxyacetate	75-100 g/l
Temperature	95°C
pH	6.0-6.5

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[1]Brenner, A. and Riddell, G. E., Proc. Am. Electroplaters' Soc., 33, 23 (1946).

Brenner, A. and Riddell, G. E., Proc. Am. Electroplaters' Soc., 34, 156 (1947).

A few deposits were obtained from five (5) sulfamate baths:

		1	2	3	4	5
Nickel sulfamate	g/l	32	32	32	50.2	50.2
Sodium hypophosphite	g/l	10	10	10	21.2	21.2
Sodium hydroxyacetate	g/l	50	50	25		
Ammonium citrate	g/l	-	-	-	100	100
Sodium citrate	g/l	-	-	25		
Boric acid	g/l	3	33	3		
Borax	g/l	-	-	-	30	30
Sodium lauryl sulfate	mg/l	-	1.5	1.5		
Ammonium hydroxide to pH for maintenance (not for make-up)					9.5	
Sodium hydroxide to pH					9.5	9.5

Several proprietary baths were used and these are identified with I, II, and III. Except as otherwise indicated, these were all operated in accordance with the vendor's instructions.

Solutions used for other than the Ni-P alloys will be identified where they are discussed.

Plating Cell

The basic plating cell was a glass cylinder of about 1.1 liter capacity containing 1 liter of solution. This was immersed in a water-ethylene glycol bath which was heated by a hot plate, a quartz immersion heater, and/or an infrared lamp. An automatic temperature control kept the temperature constant to within a degree centigrade for most of the experiments. Agitation, when used, was provided by air from fritted glass disks at the bottom of the container, or a rotating magnetic stirrer.

Continuous filtration was used for the proprietary solutions. The approximately 1 liter of solution was pumped through a 15 μm cartridge filter at the rate of 10 liters/hour. This, of course, provided additional agitation.

Schedule of Deposits

Much of the data obtained are summarized in Tables 1 to 7. Those data which had questionable validity or did not appear to be significant for the purposes of this report are not included.

Unless otherwise noted, the solution was freshly prepared for each deposit. Additions were made continuously to the Brenner solution to maintain the nickel and hypophosphite concentrations within about 10% of the initial

levels and the pH was maintained by the addition of ammonium hydroxide. Where a pH range is given with 6.6 as the maximum, the pH was not adjusted at any time. That is, the pH was 6.6 as made up and decreased with use. The pH of the replenishment solution was in the neighborhood of 6.6 and hence, there was, in effect, a continuous addition of higher pH solution.

Several of the deposits were obtained with other than the standard or normal solution and operating conditions. Some of the variations are indicated in Table 1; others are indicated here.

Deposits 1 to 7 were obtained successively from the same solution. The solution was filtered and the pH adjusted to 4.5 between each run. When deposit 7 was started, the bath had been operated 45 hours and there was an accumulation of phosphite equivalent to 12.6 g/l of sodium phosphite.

Deposit 16 was obtained with no replenishment of the solution.

Ten g/l of sodium phosphite had been added to the bath from which deposit 24 was obtained.

Deposit 29 was withdrawn from the bath after three hours of plating with continuous filtration when general decomposition of the bath began. A new bath of the same type was used for deposits 57-61 and it was much more stable.

Deposits 34-36 were obtained successively from the same bath.

During deposition of #37, the bath started to decompose after about 2 hours. Deposit 41 was subsequently deposited from the same bath after filtration and adjustment of composition.

Thirty-eight and 39 were obtained successively from the same bath and 42-45 from another bath.

Forty-six, 47, and 48 were operated normally except that no replenishment with Part C was made. Each bath started with a nickel concentration of 1.2 oz/gal (9 g/l).

Deposit	Time Hr	Final Nickel Concentration (oz/gal)	g/l
46	3-1/4	0.88	6.7
47	5	0.82	6.1
48	5	0.88	6.7

Deposits 49 and 50 were obtained from the same bath as #48 with the nickel concentration maintained at 0.88 oz/gal (6.7 g/l) with Part C.

Deposits 52-56 were from the same bath operated with different levels of hypophosphite (Part B) concentration. More details are supplied in the discussion of the effects of hypophosphite concentration on phosphorus contents of the deposits.

Deposits 57-59 were obtained successively from the same bath and 60 and 61 successively from another bath.

Decomposition

After a few hours of operation of the Brenner bath, bubbles of hydrogen begin to form at isolated points on the walls and bottom of the container especially along scratches. This occurs at more and more points with time, and nickel deposits become evident where gassing has occurred. This eventually progresses to the point where the bath becomes virtually useless. This decomposition or instability is favored by high pH, high temperature, high hypophosphite, and accumulated phosphite in the bath.

Stabilizers are usually added to proprietary baths to prevent or retard this process. With bath I the instability showed up as rapid formation of finely divided particles throughout the bath. This occurred after several hours of operation with filtration but without replenishment of Part C containing stabilizers and nickel salts. It also started to occur after two hours of operation of bath I at a higher than normal pH of 5.2.

Plating Rate

It is well known that the plating rate is dependent on the solution composition and pH and on the solution temperature. A decrease in nickel concentration, hypophosphite concentration, pH, or temperature will decrease the deposition rate. Such decreases are normally expected as a plating bath is used unless steps are taken to replenish the solution or to maintain its temperature.

Rate data is given in Table 1. These were estimated from micrometer measurements or from weight changes assuming a density of 7.85 g/cm^3.[2]

In the literature[3] there is a rule of thumb for the acid type of electroless nickel solution that a 10°C change of temperature will change the plating rate by a factor of 2. This was essentially substantiated by a series of rate measurements during deposition from the Brenner solution.

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[2]"Symposium on Electroless Nickel Plating", ASTM Special Technical Publication, No. 265, 16 (1959).

[3]"Symposium on Electroless Nickel Plating", ASTM Special Technical Publication, No. 265, 29 (1959).

Specimen	Temperature	Plating Time	Weight of Deposit	Rate of Deposition*	
20	50°C	71 hr	2.051 g	0.71 μm/hr	0.028 mil/hr
22	60	44	2.593	1.45	0.057
21	70	21	2.421	2.85	0.11
23	80	10	2.237	5.3	0.22
13	95	4-1/2	2.855	15.7	0.62

*Density assumed to be 7.85[2]

For each of these measurements a fresh bath was used and continuous additions of hypophosphite and nickel chloride were made to maintain the composition within 10% of the original nickel and hypophosphite concentrations. The initial pH was 6.6 and the final was 4.3-4.5.

Appearance and Surface Roughness

With prolonged operation of a Brenner solution without continuous filtration, the upward facing surfaces of a deposit become rough. Apparently, microscopic particles or sediment form in the solution and settle out on the work surfaces causing roughness. Eventually nickel particles are observed on the walls of the container and the nickel deposition slowly gets out of hand.

This roughening is the only detrimental change in appearance that has been observed for deposits from the Brenner bath. Roughness could probably be prevented by continuous filtration.

In the case of bath I, failure to use the replenisher solution (Part C) containing stabilizers resulted in violent decomposition of the bath with precipitation of finely divided particles even though it was being continuously filtered. This resulted after several hours of operation during which time the deposit was getting duller but not rough. The deposit would probably have gotton rough if it were allowed to remain in the bath after decomposition began. It appears that a "bright" electroless nickel will lose its brightness if the bath is not properly maintained.

When the Brenner bath was operated at low temperature, the deposit was substantially brighter than normal. The effect was noticeable even at 80°C as compared with 95°C.

All the deposits from the sulfamate baths were full bright, comparable to the proprietary bright baths.

Structure and Composition

Electroless nickel deposits, prior to heat treatment, do not have a grain structure which can be seen microscopically. If properly etched, however, a cross section will exhibit a banded or straited appearance. This is associated with variations in the phosphorus content and has been mentioned in the literature. This interpretation of the striations was verified by scanning a cross section for phosphorus with an electron probe. The dark layers or more heavily etched layers corresponded with layers of low phosphorus content. This is described more fully in Appendix A which has been published.[4]

Phosphorus Content

Usually a weighed sample of the electroless nickel was analyzed only for nickel by the conventional dimethylgloxime method. The remainder was considered to be phosphorus. Early in the investigation, the phosphorus was also determined gravimetrically as ammonium phosphomolybdate. Because the nickel and phosphorus determinations added up to 100.0 ± 0.1%, the more difficult phosphorus analysis was usually omitted.

The phosphorus content of a number of deposits was determined because of its recognized importance to their mechanical properties. Its dependence on solution pH is well recognized and the Electroplating Engineering Handbook[5] indicates that increasing the hypophosphite or phosphite concentration in the bath also favors increased phosphorus in the deposit.

The data in Table 1 are in agreement with these observations. The effect of pH is illustrated by deposits 14 and 19. With a pH range of 4.2-4.5, the deposit was 10.1%P. At the higher pH range of 4.5-6.6, the phosphorus was lower at 8.7%.

Comparison of deposits 7 and 14 show the effect of accumulated phosphite in the bath. Deposit #7 was from a bath which had been used for about 45 hours and had accumulated phosphite equivalent to 12.6 g/l of sodium phosphite. (Deposits 1 through 6 came from the same bath with filtration and pH adjustment at the end of each run and continuous addition of nickel and hypophosphite replenishment solution.) Deposit 7 contained 11.1%P and deposit 14, 10.1%P.

The effect of accumulation of phosphite in bath I is shown by deposits 42-45. The phosphorus in the deposits increased from 7.4 to 9.6%P during 19 hours of operation of the bath with replenishment as recommended.

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[4]Ogburn, F. and Johnson, C. E., Plating 60, 1043 (1973).

[5]Graham, A. K. Ed., Electroplating Engineering Handbook, Van Nostrand Reinhold Co., New York, 3rd Ed., 497 (1971).

The effect of hypophosphite content of the bath is illustrated by deposits 42, 43, and 55 (normal hypophosphite content), deposits 53 and 54 (low hypophosphite content), and deposit 56 (high hypophosphite content). Deposits 42 and 43 were successive deposits from a new bath I and were 7.4 and 8.2%P respectively. Another new bath I was operated 9 hours in the normal manner but without addition of the Part B replenishment solution (deposit 52). At the end of the 9 hours, chemical analysis indicated a reducer level of 2.1 fl. oz/gal. Deposits 53 and 54 with 7.0% and 7.2%P were obtained from the same solution over a period of 24-1/4 hours during which time normal replenishment with Part B was made to hold the low hypophosphite concentration constant. The hypophosphite concentration was then restored by addition of Part B to the 9 fl. oz/gal level and deposit 55 was obtained over 5-1/3 hours. The last deposit, #56, with 10.1%P, was obtained during five hours of operation with normal Part B replenishment, but after bringing the reducer level to 13.7 fl. oz/gal. The association of phosphorus content with reducer level is obvious.

Deposit	Time Hr	%P	Part B (Reducer) Level fl oz/gal
	New Bath I:		
42	4-1/2	7.6	9
43	4	8.2	9
	Another New Bath I without continuous Replenishment with Part B:		
52	9	-	9-2.1
	Continuous Replenishment of Depleted Bath with Part B:		
53	12-1/4	7.0	2.1
54	12	7.2	2.1
	Normal Concentration of Reducer Restored:		
55	5-1/3	8.7	9.0
	Concentration of Reducer Increased:		
56	5	10.1	13.7

The relation of phosphorus to temperature of deposition is also of interest.

Deposit	Bath Temperature °C	Deposition Time Hr	Rate of Deposition mils/hr	%P
20	50	71	0.03	12.5
22	60	44	0.06	11.9
21	70	21	0.1	11.1
23	80	9-1/2	0.2	10.0
19	96	5-1/2	0.5	8.7

The deposition time was selected so that the deposit thickness for each would be about the same. It is apparent that the phosphorus content is related to the deposition temperature. Part of the effect might be due to build up of phosphite during the longer runs at low temperature, but this seems unlikely. The amount of nickel deposited would not have differed much from run to run and the phosphite build-up would probably be about the same each time.

For each of these measurements, a fresh bath was used and continuous addition of a replenishment solution was made to maintain the solution composition within 10% of the original nickel and hypophosphite concentrations. The initial pH was 6.6 and the final was 4.3-4.5.

Low Phosphorus Alloy

Baths II and III were obtained because the vendors advertised a low phosphorus content for the deposits, 2% or less. Both baths were operated in accordance with the vendor's instructions, but deposits from both were high in phosphorus, 12% and 12.3%. Both vendors were contacted and informed of our experience. One vendor said they had replaced the low phosphorus bath with a high phosphorus bath without changing the trade name or designation. The other vendor sent us more of their bath which gave us the same results. We sent them a sample of our deposit from this second lot and they confirmed our analysis of phosphorus 12.3%, and sent us still more of their bath, but we did not use the last lot.

One reason for using the alkaline sulfamate bath was the report that deposits from it were 2 to 3% phosphorus.[6] Our deposits, numbers 80-82, were 5.2, 5.5, and 6.5%P. To obtain deposits with low phosphorus content we used the modified Brenner bath with high nickel and low hypophosphite content and a pH of 6.0-6.6. This gave deposits with 2.8% and 3.7% phosphorus and they were relatively ductile.

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[6]Cadorna, L. and Cavalotti, P., Electrochemica Metallorum 1, 93 (1966).

Hardness Measurement

All hardness measurements were made with a Knoop indenter using a Tukon microhardness tester. The indentations were made on cross sections with the long axis parallel to the substrate. The location of the indentation was such that it was not influenced by the proximity of either boundary of the deposit or of another indentation. Some indentations led to the formation of microcracks particularly with loads of 500 g. These were not measured for hardness values and new indentations were made with a lighter load.

The specimens for hardness measurement were mounted in an epoxy cement cured at room temperature so as to avoid any heat effects. The heat involved in normal mounting in Bakelite or Lucite would have had serious effects on the subsequent hardness measurements. After grinding and polishing, the specimens were etched just sufficiently to bring out indications of the usual striations. Heavier etching leads to low hardness values and can be seriously misleading. Even such a light etch has significant effects. Unfortunately this was not realized until after a number of the measurements reported here had been made. Light polishing after the light etch may increase the measured hardness by about 35 units when a load of 100 g is used. This technique was followed for deposit 34 and all subsequent deposits. The hardness values reported for all preceding deposits have been increased by 35 units.

Each hardness value reported is the average of one measurement of each six indentations. The cross sectional specimen was about 1/2 inch long and three indentations were made near either end. All measurements were made after the operator had checked his technique with a standard hardness block. The precision of the operator's measurements was the subject of a brief evaluation. The standard deviation for a single measurement was 1.4% and for an average of six measurements it was 0.57% based on 430 degrees of freedom. This precision is meaningful only for measurements on a single specimen such as measurements before and after various heat treatments. It is not a measure of the reproducibility of specimens and is not applicable when comparing one specimen with another.

Also the measurement precision is undoubtedly much poorer at low loads of 25 and 50 g.

The hardness of an electroless nickel deposit is not uniform. It varies from place to place, presumably as the composition or phosphorus content varies. This was evident when the hardness of a lightly etched specimen was measured on both a dark (etched) band and on a light band. The etched band measured 526 HK_{200} and the light band measured 483 HK_{200}. Smaller, but significant differences were also noted between the two ends of several mounted specimens. As noted earlier, three measurements were made at either end of each specimen and the indentations were made in the same position relative to the banded etch pattern.

Initially, hardness measurements were made with a 500 g load. Later it was found that some of the specimens which had been heat treated at 400°C cracked when the indentation was made. It was found that with a 100 g load cracking was not a problem and all subsequent measurements were made with a 100 g load.

In order to convert our own data from one load to another, a number of specimens in several different hardness ranges were measured with 25, 50, 100, 200, and 500 g loads. This data was combined to produce a graph which could be used to convert data for one load to values approximating what would have been obtained at another load. Such a conversion graph has been helpful, but its use, even by the same operator using the same equipment, introduces some error. The use of this specific graph by another laboratory would be questionable. Too much depends on the surface preparation of the specimen, on the operator's technique, and on the hardness measuring equipment. Most of the hardness values given in this report as HK_{100} were measured with a 100 g load. Some, however, were measured at other loads and the values converted to those for 100 g loads.

Heat Treatment

Heat treatments were made simply by placing the specimens in an oven already at the desired temperature and holding the temperature for the desired time interval. Each specimen was allowed to cool in room temperature air. For hardness measurements, the specimens were metallographically mounted after heat treatment and cooling to room temperature except those specimens treated at 100 and 200°C. These specimens were mounted before heat treatment and successively treated for the desired time intervals. Thus for heat treatments at the same temperature only one mounted specimen was usually used for the successive time intervals. The heat treatment times recorded are the times in the oven and include the time required to bring the specimen to temperature. Because the specimens were thin, about 30 mils, they probably reached temperature in a very short time; insignificant except for periods of less than 15 minutes.

Hardness of Ni-P Alloys

The hardness data for the Ni-P alloys are summarized in Tables 2 to 7 and Figures 1-6. These data include hardnesses as-plated and after heat treatments of 1/2 hour to 9 days at temperatures of 100°C to 800°C. Also these data are for deposits from all the baths mentioned earlier and most of these had been operated at more than one composition and under several different operating conditions. Thus these data represent a variety of electroless Ni-P deposits.

As-plated hardness of deposits are given in Table 2 and most of that data is plotted in Figure 1. The scatter of that data may be due, in part, to the nonuniformity of each deposit and to imprecision of measurement. Much of the scatter, however, is real and indicates that the phosphorus content is not the only feature of electroless nickel that influences its hardness. The deposition process (plating bath) must influence the structure of composition of the deposit.

For phosphorus concentrations above about 7%, there does not appear to be any significant relation between phosphorus content and as-plated hardness. Most of the hardnesses are within a range of 500-600 HK_{100}. Below 7%, the deposits tend to greater hardnesses with 732 the hardest we measured.

The Electroplating Engineering Handbook[5] gives a range of 100 DPH for as-plated deposits. Since most electroless nickel coatings have more than 7% phosphorus, that statement is reasonable though not complete. Graham et al[7] reported that for a specific, well-controlled, alkaline bath, the hardness of the deposits decreased from 560 to 530 KHN with a corresponding phosphorus increase from 4.5 to 9.5%. Any such trend in our deposits would be obscured by other variables. Randin and Hinterman[8] using an acid solution show a pronounced minimum in hardness at about 6.3% phosphorus. This minimum does not appear in our data. Their data, when compared with ours, emphasize that hardness is influenced by more than just phosphorus content.

Table 2 and Figure 1 also give data for hardness after heat treatments of eight hours at 200°C and 1/2 hour at 400°C. In Figure 1, the points on any one vertical line are for the same deposit. For the 200°C heat treatment there is a clear trend to lower hardness with increasing phosphorus content. Generally the 200°C treatment increases the hardness, but for some of the deposits with 10% or more of phosphorus, the hardness decreased. During the 400°C heat treatment, the hardness increased to 840 to 1001 HK_{100}. One exception was the specimen with 2.8% with a hardness of 812 HK_{100}, less than after the 200°C heat treatment. No trend of hardness with phosphorus content was evident.

The data of Table 2 and Figure 1 raise the question of what would the data look like after different heat treatment times. Was the hardening process complete? Consequently, data on hardness changes with heat treatment with time were obtained. Starting with storage at room temperature, 19-23°C, for two years, a decrease in hardness was observed for one low phosphorus specimen and no significant change for two others.

%P	As-Plated	After 2 Years
4.5	732 HK_{100}	652 HK_{100}
7.1	602	607
12.5	536	542

[7]Graham, A. H., Lindsay, R. W. and Read, H. J. J. Electrochem. Soc., 112, 401 (1965).

[8]Randin, J. P. and Hinterman, H. E., Plating, 54, 529 (1967).

At 100°C, measurements were made over periods of up to nine days. These data are in Table 3 and Figure 2. Significant changes occur at that temperature, but at greatly varying rates. A specimen with 4.5%P has completed the hardening process in one day. Those with 7.1% and 12.5% took much longer and may not have completely hardened after nine days. One specimen decreased in hardness and another showed no change. Our data is not sufficient to establish any pattern or correlation.

Heat treatments at 200°C were also conducted for periods up to nine days. Most of the hardness changes took place within one day, but it is not clear that the changes were complete within the nine days. See Table 4 and Figure 3. Of interest are the four specimens with 12.2% or more phosphorus. Initially these decreased in hardness reaching a minimum between two and eight hours and then recovering to a hardness which was sometimes more and sometimes less than the initial hardness. This dip in hardness corresponds to the decrease in hardness recorded in Table 2 and Figure 1.

Figure 3 shows a small dip in hardness between one and nine days of heat treatment at 200°C. The dip is very shallow; but because the hardness measurements for each deposit were made on identical specimens, by the same operator, with the same equipment; we believe the dips to be real.

Data for hardness vs. time at 400°C are given in Table 5 and some of them are used to construct Figure 4. In Figure 4, where the 0 and 1/4 hour points are connected by straight lines, the hardness rapidly increases and then abruptly levels off or slowly decreases. We do not know where the break occurs. Higgs[9] observed that this break occurred within five minutes or perhaps even one minute. Two of the deposits with 4.5 and 6.8%P did not show that abrupt change, but continued to increase in hardness for at least two hours. Again it is apparent that the properties of electroless nickel do not depend solely on phosphorus content.

The data in Table 6 and Figure 5 show hardness changes with duration of heat treatment at 600°C. During the first 1/4 hour, the hardness increases quite rapidly and then abruptly levels off or decreases. As with the 400°C heat treatment, we do not know just when this break occurs. Specimens from deposit 56 with 10.1%P, heated for two and four minutes, had hardnesses of 948 and 894 HK_{100} respectively. These heating times are not to be taken too seriously as they include an unknown time for bringing the specimens up to temperature. They suggest, however, a very rapid rise and fall of hardness during the first few minutes of heating.

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[9]Higgs, C. E., Electrodeposition and Surface Treatment, 2, 315 (1973-74).

Subsequent to the period of rapid change, the hardness of most of the specimens changed slowly and went through a maximum after about one hour. The low, 2.8%, phosphorus specimen quickly softened initially and then showed no further change.

In Figure 6, hardness is plotted against the temperature of a 20 hour heat treatment for specimens with several different phosphorus contents. Table 7 gives the data for these curves and also gives equivalent data for one hour heat treatments. The two sets of data are sufficiently similar that preparing a graph for the one hour data is not helpful. With intermediate percentages of phosphorus, the hardness increases with temperature of heat treatment until a maximum is reached near 400°C. Above 400°C there is a sharp drop in hardness. For the 12.5%P, the drop is much less for temperatures above 400°C. With 2.8%P, the maximum comes somewhere between 250 and 350°C.

The curves of Figure 6 are reminiscent of, but substantially different from, those published by Gutzeit and Mapp,[10] Baldwin and Such,[10] and Higgs[9] for one hour heat treatments of specimens with 8 to 9% phosphorus. The differences are attributable to the duration of heat treatment, phosphorus content, and, more importantly, the conditions of deposition. Of practical significance is the temperature of maximum hardness and how critical the temperature is. Gutzeit and Mapp[10] and Higgs[9] gives the temperature for maximum hardness at 400°C. Baldwin and Such[10] found it to be nearer 350°C. Our data shows a maximum nearer 300°C for 2.8%P, but within 410 ± 15°C for deposits of the higher phosphorus contents. The sharp drop off of hardness with temperatures could change the hardness substantially. With one hour treatments, this hardness decrease seems to be less severe, but still could be significant. If the heat treatment temperature is to be designated in procurement specifications, the danger of going to too high a temperature should be considered. It would be advisable to determine the minimum temperature at which a sharp drop can occur.

The hardening of the nickel-phosphorus alloy when it is heated to 400°C is attributed to a phase change from a solid solution of phosphorus in the nickel to a finely divided precipitate of a nickel-phosphorus compound (usually considered to be Ni_3P) in a nickel matrix or to the formation of nickel particles within a matrix of the nickel-phosphorus compound. Subsequent softening after further high temperatures is attributed to growth of the nickel grains with segregation of the compound. It is unlikely that these processes are responsible for all the hardness maxima and minima that appear in the plots of hardness vs. heat treatment time and temperature. What other processes are involved is not known, but possible ones are stress relief, expelling of hydrogen, and interaction with other impurities.

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[10]Gutzeit, G. and Mapp, E., Corrosion Tech., 3, 331 (1965).

Baldwin, C. and Such, T. E., Trans. Inst. Metal Finishing, 46, 73 (1968).

Adhesion

No systematic investigation of adhesion was made. A number of test specimens were prepared according to the schedule in Table 8. These test specimens were 1/8 inch steel rod, plated with about 1 mil (25 μm) of electroless nickel. They were sent to Rock Island Arsenal to be tested by the Beams high-speed rotor method.

To find conditions for obtaining adhesion of electroless nickel to Cr-Mo-V steel (gun stock), 10 wafers of the steel were prepared according to the schedule in Table 9 and plated with electroless nickel from solution I. One half of each wafer was tested as-plated for adhesion and one half after one hour at 400°C. The test consisted of making a right angle bend around a 1/8 inch diameter mandrel and visual examination for separation of the coating from the steel. The results are tabulated in Table 9. The best adhesion was obtained with an $Al(NO_3)_3$-HCl pickle at 42°C[11] followed by a lactic acid-peroxide desmutter at room temperature.[11] Usually one hour at 400°C improved the adhesion and never did it result in poorer adhesion.

If such pretreatments are to be used for gun bores, one should know the amount of metal removed. This proved to be close to 0.4 mil (10 μm). When the pickle and desmutter were used at room temperature for the same time periods, the metal removed was 0.005 mil (1.2 μm) and subsequent adhesion of a deposit from bath I was not adversely affected.

Wear Tests

A few wear tests were made to compare chromium (standard bath at 30 A/dm^2 and 55°C) with nickel-8.5% phosphorus from bath I. The data from these tests with a Taber Abraser are summarized in Table 10.

These wear tests were made with CS-17 and CS-10 wheels with a load of 1000 g. A track was worn into each specimen prior to the test runs by making several runs of 2500 cycles each. Several test runs were then made on each specimen and the average weight loss or thickness loss is reported. CS-17 wheels were used initially. Subsequently we found that the CS-10 wheels were less prone to load-up with metal powder and gave more consistent data.

The data in Table 10 indicate that the 400°C heat treatment improved the wear resistance of the electroless nickel-phosphorus. Electrodeposited chromium, however, was still more wear resistant. This may be indicative of service performance, but we do not know how this test correlates with service life.

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[11] U. S. Patent 3,505,095; April 7, 1970 assigned to U. S. Atomic Energy Commission by G. S. Petit and R. R. Wright.

Plating of Gun Bores

Prior to plating .177 caliber gun bores, the bore of a 20 inch length of 3/16 inch I.D. steel tube was plated with 0.7 mil (18 μm) electroless nickel from bath I to determine what metal distribution problems there might be. From microscopical examination of cross-sections of the deposit, it was determined that there was no significant variation of coating thickness from end to end or circumferentially.

The set-up used for plating the gun bores is indicated in Figure 7. Once the barrel was in place, the complete plating cycle was carried out by appropriate manipulation of stop-cocks and pumps. Continuous additions were made to the electroless nickel bath in a 2 liter reservoir where automatic temperature control was maintained. The plating solution was continuously filtered.

Initially the bore was swabbed with benzene soaked gun patches and then it was put in place. The $Al(NO_3)_3$-HCl pickle was pumped through the barrel for four minutes, cold tap water for one minute, and lactic acid-peroxide desmutter for two minutes, all at room temperature. A cold water rinse for one minute was then followed by the electroless plating bath.

Four barrels were plated using bath I at 89°C with the pH at 4.8. They were delivered to Rock Island Arsenal. Attempts to plate barrels from bath III were completely unsuccessful. No deposit at all was obtained. This bath was operated at a pH of 5.8 at 90°C and two widely different flow rates were tried. Because barrels could be plated with another proprietary process, no real attempt was made to find suitable operating conditions for this bath. Presumably this is an example of the detrimental affects of excess agitation of electroless nickel-phosphorus baths with catalytic-poison stabilizers.[12]

Electroless Ni-P-Cu Alloy

A deposit was obtained from a bath containing:

Nickel sulfamate	100 ml/l (7.5 g/l Ni)
Copper sulfamate	0.65 ml/l (40 mg/l Cu)
Sodium hydroxyacetate	50 g/l
Sodium hypophosphite	10 g/l
Sodium lauryl sulfate	1.5 gm/l
Boric acid (present in sulfamate)	3 g/l

[12] Lowenheim, F. A., Ed., Modern Electroplating, Wiley-Interscience, New York, 3rd Ed., (1974).

We believe the deposit from this bath contained a small amount of copper, but we did not verify this. Deposition was carried out for 4-3/4 hour at 95°C with continuous filtration and continuous addition of nickel, copper, and hypophosphite. The initial pH was 6.2 and the final was 4.8. The deposition rate averaged 0.5 mil/hr and the final deposit was brittle. The Ni-P-Cu and the Ni-P deposits from the sulfamate bath seemed to be of equal brightness, but the surface texture of the Ni-P-Cu deposit, when viewed microscopically, appeared to be much smoother than the Ni-P deposit. It appeared that some leveling had occurred.

Hardness was measured after 1 hour heat treatments:

As-plated	548 HK_{25}
400°C	960 HK_{25}
600°C	771 HK_{25}
800°C	491 HK_{25}

Ni-P-Mn Alloy

Because a small amount of manganese codeposited with nickel stabilizes the hardness of nickel during heat treatments at 450°C,[13] we attempted to codeposit manganese with electroless nickel-phosphorus. Two sulfamate baths, differing only in the concentration of manganese sulfate, were tried.

Nickel (added as nickel sulfamate)	7.5 g/l
Manganese (added as manganese sulfate)	1.4 and 2.8 g/l
Sodium hypophosphite	10.0 g/l
Boric acid	3.0 g/l
Sodium hydroxyacetate	50.0 g/l
Sodium lauryl sulfate	1.5 mg/l

With 2.8 g/l of manganese in the bath, the average deposition rate over a period of 5 hours was 0.2 mil/hr. (5 µm/hr.). The initial pH was 5.7 and dropped to 3.8. The deposit, steel gray in color, was too brittle to use a load of 50 g or more for hardness measurements and contained about 1% manganese. The bath with 1.4 g/l of manganese deposited at a rate of 0.3 mil/hr. (8 µm/hr.) and gave full bright deposits containing about 0.05% Mn. These were also quite brittle.

[13] Stephenson, Jr., Plating 53, 183 (1966).

Portions of these Ni-P-Mn deposits were heated for 1 hour at various temperatures, allowed to cool in air, and measured for hardness with a 25 g load.

	Low Manganese HK_{25}	High Manganese HK_{25}
As-plated	489	485
400°C	649	768
500°C	769	
600°C	791	931
700°C	811	
800°C	574	

The manganese apparently increases the heat treatment temperature for maximum hardness, but without increasing the maximum hardness. No data was obtained to relate hardness to the duration of heat treatment.

Electroless Nickel-Boron

There is some interest in electroless nickel-boron coatings because they are harder than the nickel-phosphorus deposits and the changes undergone during heat treatment are somewhat different. Electroless nickel-boron baths were not extensively investigated in the course of this project, but a few deposits were obtained from several different baths including both borohydride and dimethylamineborane types. The formulation of the various baths are given in Table 11.

Bath 1 proved to be rather unstable. At 90° it decomposed spontaneously but slowly with the formation of metallic particles. At 80°, with continuous filtration through a 1-3 µm polypropylene filter, decomposition became evident after one hour of operation.

Bath 2 was used by Gorbunova et al.[14] It differs from bath 1 by an increase of thallium nitrate from 7 to 100 mg/l. Deposits were obtained from this bath at 80, 90 and 95°C. At the lower temperature they were dark gray with some roughness and the plating rate was 0.5 mil/hr (13 µm/hr.). At 95°C the plating rate was 1 mil/hr (25 µm/hr.) and the deposits were a silvery gray and smooth. The hardness tabulated below were measured as-plated and after a single heat treatment at each of several temperatures.

[14]Gorbunova, K. M., Ivanov, M. V., and Moiseey, V. P., J. Electrochem. Soc., 120, 613 (1973).

	Deposited at 95°C		Deposited at 80°C
	HK_{50}	HK_{25}	HK_{25}
As-plated	764	842	854
400°C	979	1272	1245
600°C	907	983	
800°C	976		

We found that when this high pH bath was operated at 90° or 95°C, the internal bushings of our pump would swell and seize. At 80°, this was not a problem.

Bath 3. This bath ceased to function after about five minutes. It is possible that it was poisoned by the stop-off used on the steel work piece or the lead ion concentration was too high.

Bath 4 was given in a technical bulletin of the Callery Chemical Company. This bath operated 1-1/2 hours and then stopped plating. We did not attempt to determine the reason plating stopped or to make up a new bath. The plating rate was 0.7 mil/hr (17 µm/hr.) and the deposit was a silvery gray, stressed, and quite brittle.

	Hardness
As-plated	777 HK_{25}
1 hr. at 400°C	1198
1 hr. at 600°C	1095

Bath 5 is given in U. S. Patent 3,738,849 (June 12, 1973), H. E. Bellis assignor to E. I. DuPont de Nemours and Co. The plating rate measured 0.4 mil/hr (10 µm/hr.). Surface roughness began to appear after 3-1/2 hours of operation. The deposit was dull gray and was analyzed at 95.4% Ni. Its hardness was 754 HK_{50}, as-plated.

This sampling of electroless nickel-boron is not comprehensive, but it does suggest that as-plated the hardness is more than nickel-phosphorus deposits with the possible exception of some with 2-4 1/2% phosphorus. After one hour at 400°C, the hardnesses of the two types of electroless nickel do not differ significantly. After one hour at 600°C, however, the boron alloy retains a much greater hardness than the phosphorus alloy. Gorbunova et al show that a plot of hardness vs temperature of heat treatment has two maxima, at 300°C and 600°C, with a minimum at 400°C for alloys of 5.7 and 6.4% boron. 4.3% boron has one maximum at 300°C.

Thickness Uniformity

The Electroplating Engineering Handbook[5] states: "Electroless plating is of uniform thickness on all areas of the solid part, regardless of its shape or geometry." In the context of electroplating this may be a reasonable statement, but it is misleading. Just how misleading was the subject of some consideration.

The rate of deposition is a function of temperature and solution composition. A systematic variation in either will usually lead to a corresponding variation in thickness. This means that to achieve a uniform deposit thickness, the average solution composition and temperature everywhere over the surface must be kept the same. Since this can be very difficult to achieve, it raises the question of how nonuniform a deposit is likely to be. The results of a few experiments made during the course of this project will give a feel of the sort of nonuniformity to expect.

The exterior of a one inch diameter brass tube was plated 2 hours without agitation, while suspended in a horizontal position well off the bottom of the container. The plated tube was sectioned near its center and examined microscopically around the circumference. At the bottom the deposit thickness was 0.68 mil, at the sides it was 0.75 mil, and at the top it varied from 0.52 to 0.88 mil. This variation at the top was associated with deposit roughness presumably caused by settling of microscopical sediment formed in the bath. The lower value of 0.52 mil probably represents the thickness that would have prevailed if there had been no sediment.

Figure 8 is a photomicrograph of a section of one of two brass bolts plated for 2 hours in the Brenner bath without agitation and while suspended by a wire. The plating rate was about 0.6 mil/hr. The electroless nickel deposit is the layer between the brass substrate and an overplate of electroplated nickel. The deposit thickness was measured at the top and bottom of the thread at six different "threads" (12 locations). There was a 6% variation between peaks compared to a 71% variation between valleys. The average peak to valley thickness ratio was 2.1. Obviously solution replenishment in the valleys was not as good nor as uniform as at the peaks.

Figure 9 is a section of another bolt plated 2 hours in bath 1 at a slower rate, about 1/3 that of the bolt in Figure 8, 0.2 mil/hr. Six valleys varied from 0.38 to 0.40 mil. Six peaks varied from 0.44 to 0.50 mil. The ratio of the two averages was 1.2. The improved throwing power may have been influenced by the bath composition, but it may also be due to the slower rate of deposition which permitted faster solution replenishment relative to deposition of nickel.

Figure 10 is of a bolt plated near the faster rate in bath 1 with agitation from a magnetic stirrer and from solution pumped in and out of the tank. The thickness ratio of peak to valley is 1.013, hardly significant. This good throwing power is attributable to appropriate agitation.

The deposit shown in Figure 11 was on a 4 mil diameter wire plated in bath 1 at the same time as the bolt with uniform metal distribution. It is obvious that the metal distribution is not uniform. The maximum thickness ratio is 1.25. Apparently the agitation did not even out the metal distribution on the wire as it did for the bolt. The wire was suspended in the bath in a manner which permitted it to move with the solution within a revolving agitation pattern. The metal distribution probably reflects a net motion between the wire and solution resulting in unequal solution replenishment.

Summary

The coating characteristics considered in this report, i.e., appearance, roughness, hardness and thickness, can be discussed in terms of process variables.

Appearance and roughness can be readily observed and an evaluation is easily made provided the requirements are adequately stated. Solution agitation and filtration are important here to prevent settling of the sediment on the work surface. To minimize formation of the sediment, the bath needs to be properly controlled, primarily by replenishment of the stabilizers and avoiding the conditions which favor solution instability such as too high a temperature, too high a pH, too much hypophosphite, and too much phosphite. The latter is a matter of the working life of the bath. Phosphite continuously accumulates and promotes formation of sediment and bath deterioration.

On the basis of the data given here along with that in the literature, several generalizations can be made about the hardness of electroless nickel deposits.

1) Most deposits will have about the same as-plated hardness. Those with less than 7-1/2%P are likely to be harder.

2) Heat treatments at 200°C is not likely to be detrimental though a few coatings with high phosphorus content may become a little softer. Some deposits may increase significantly in hardness.

3) Heat treatments at 300°C and 400°C will harden the deposit.

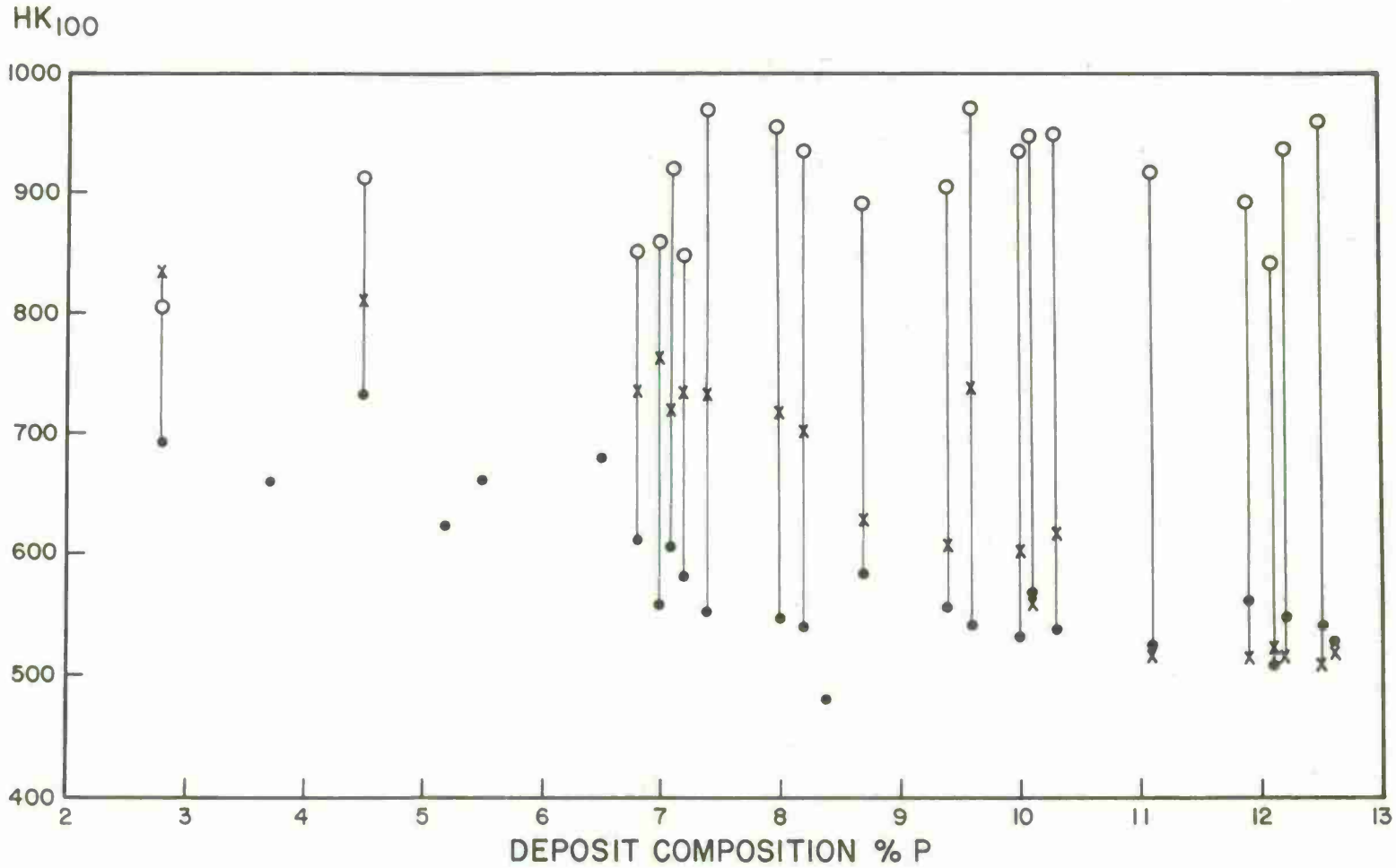
4) The optimum temperature for a one hour heat treatment of a specific deposit may be anywhere between 250 and 425°C, but will usually be between 350 and 425°C. Heating above 420°C is likely to give hardnesses significantly less than the maximum unless the phosphorus content is above 12%.

Tensile strength and ductility are important to applications of electroless nickel. These properties were measured by Graham et al[7] for deposits with 4-3/4 to 8-3/4%P after heat treatment at 200, 400, 600, and 750°C. In general these two properties increase with increasing phosphorus in the as-plated condition and after heating at 200°C. After heating at 400°C, all the deposits are very brittle and quite weak.

To control the properties of electroless nickel, it may be desirable to control the phosphorus content. This requires chemical analysis of the deposit and good control of temperature, pH, and bath composition. To assure a low or a high phosphorus content should not be difficult, to assure an average composition within 1 percentage point requires more than the normal attention to detail.

The control of deposit thickness can offer problems. Usually its measurement can only be made by microscopical techniques. The thickness can be estimated from the time of plating provided the solution is kept under close control and the plating rate is determined independently. Sometimes the total thickness of the item being plated can be measured with a micrometer before and after plating. A more generally applicable procedure is to plate a coupon simultaneously with plating of a workpiece. Appropriate weight and area measurements or microscopical measurements of the deposit on the coupon would provide a reasonably good plating thickness estimate.

Generally, the coating thickness is fairly uniform over the workpiece but such uniformity cannot always be assumed. A 2-to-1 variation can occur as in recessed areas where solution depletion takes place. Agitation can often but not always improve the coating uniformity.



as-plated x after 8 hours at 200°C o after 1/2 hour at 400°C

FIGURE 1 HARDNESS OF Ni-P ALLOY

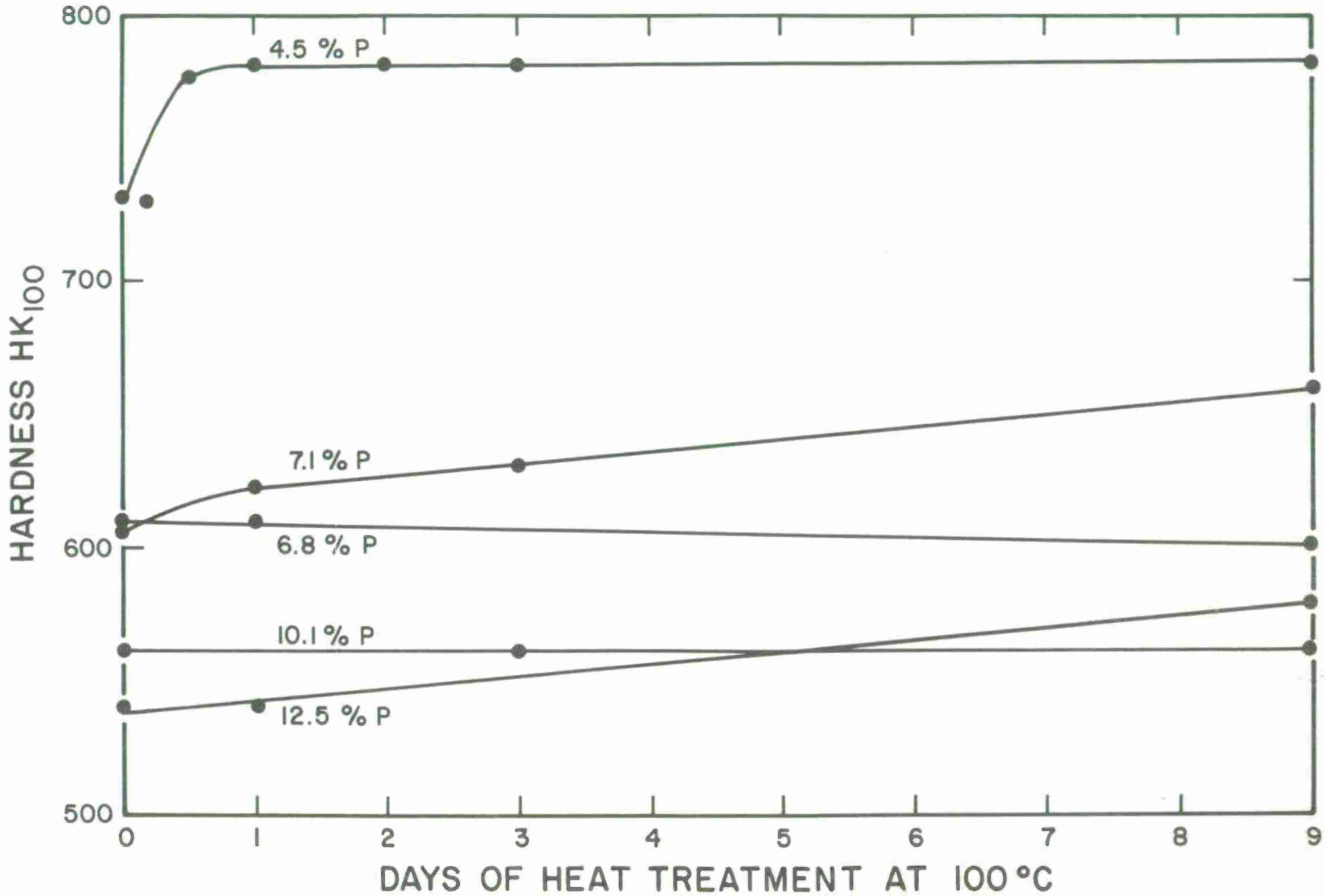


FIGURE 2 EFFECT OF DURATION OF HEAT TREATMENT AT 100°C ON HARDNESS

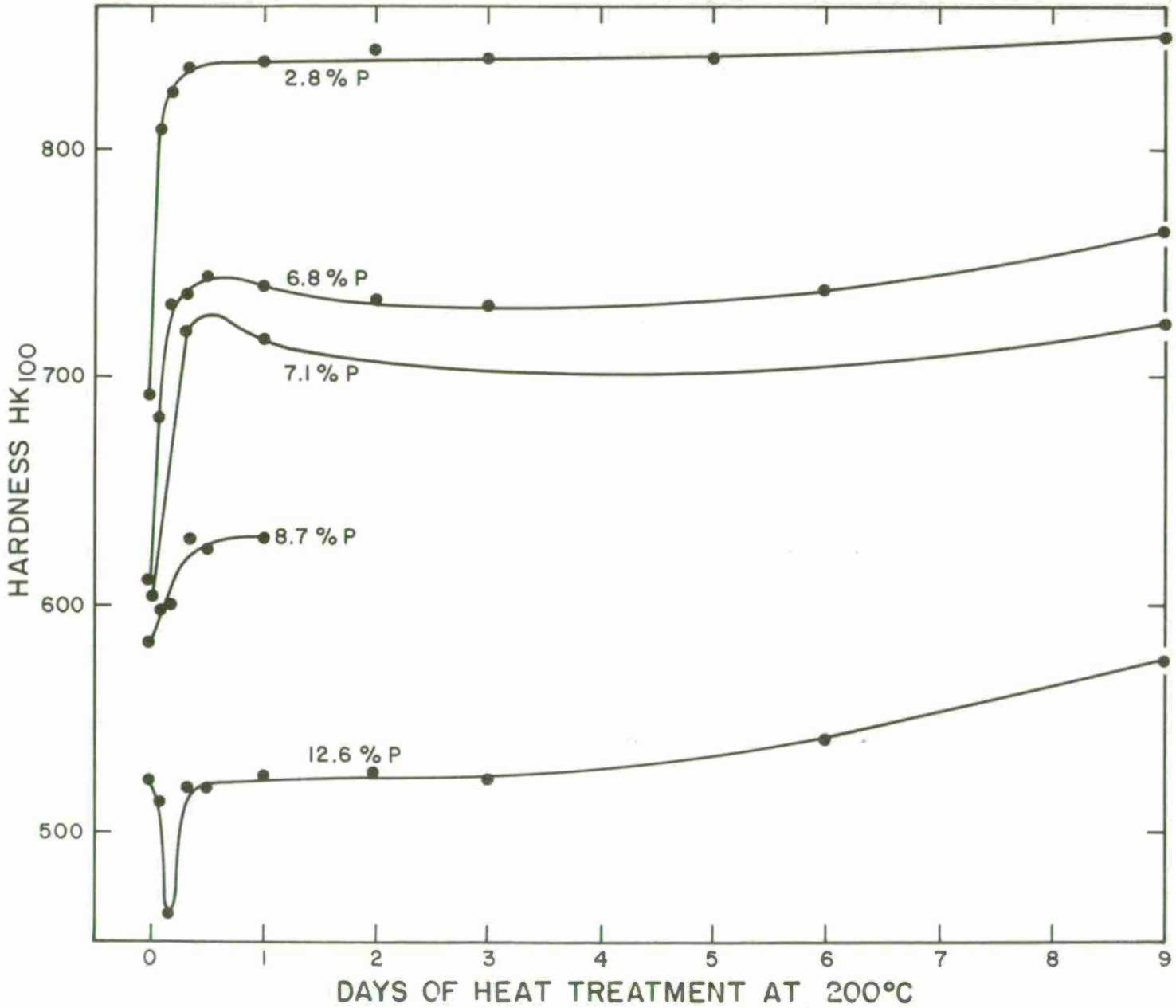


FIGURE 3 EFFECT OF DURATION OF HEAT TREATMENT AT 200°C ON HARDNESS

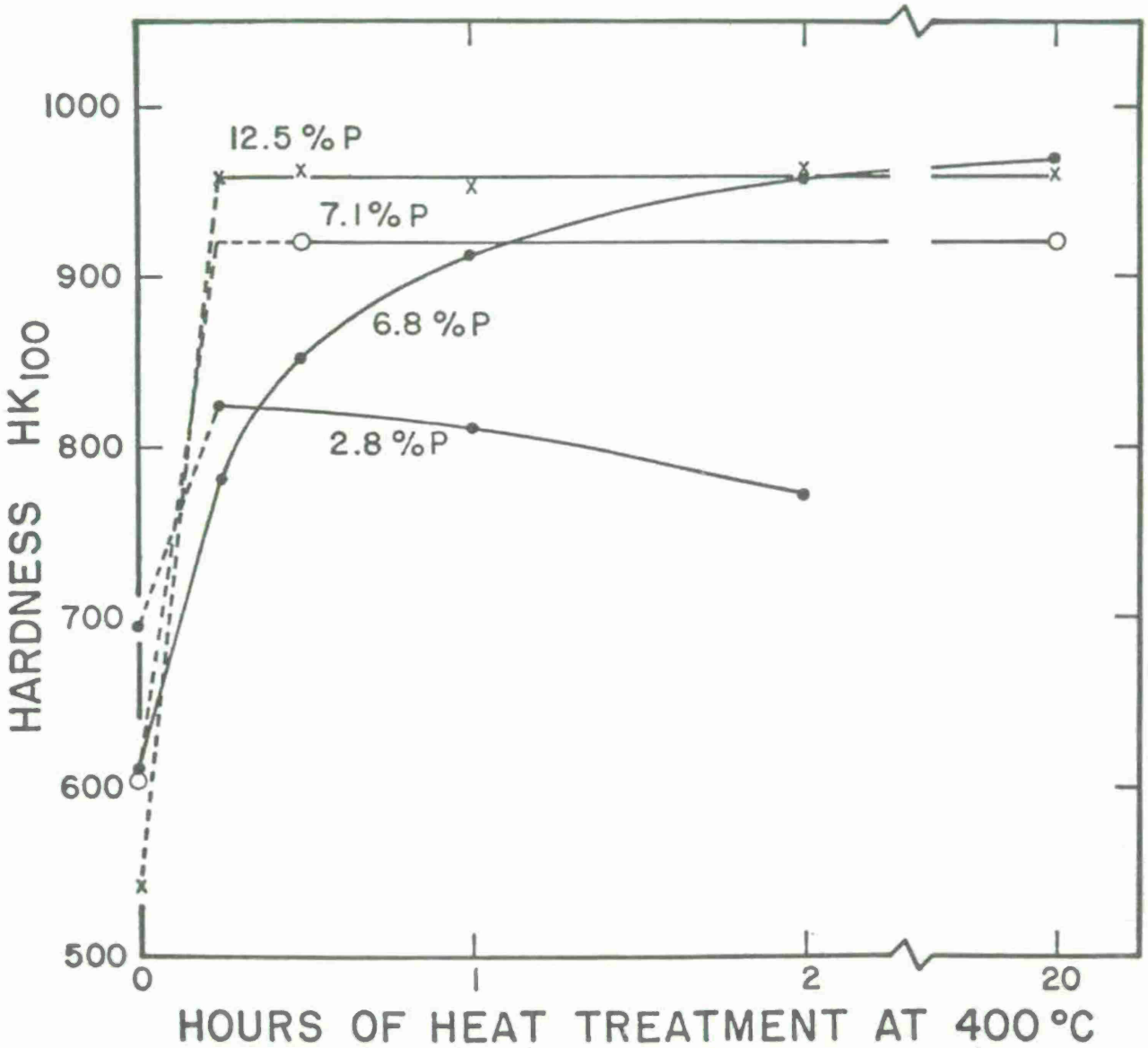


FIGURE 4 EFFECT OF DURATION OF HEAT TREATMENT AT 400°C ON HARDNESS

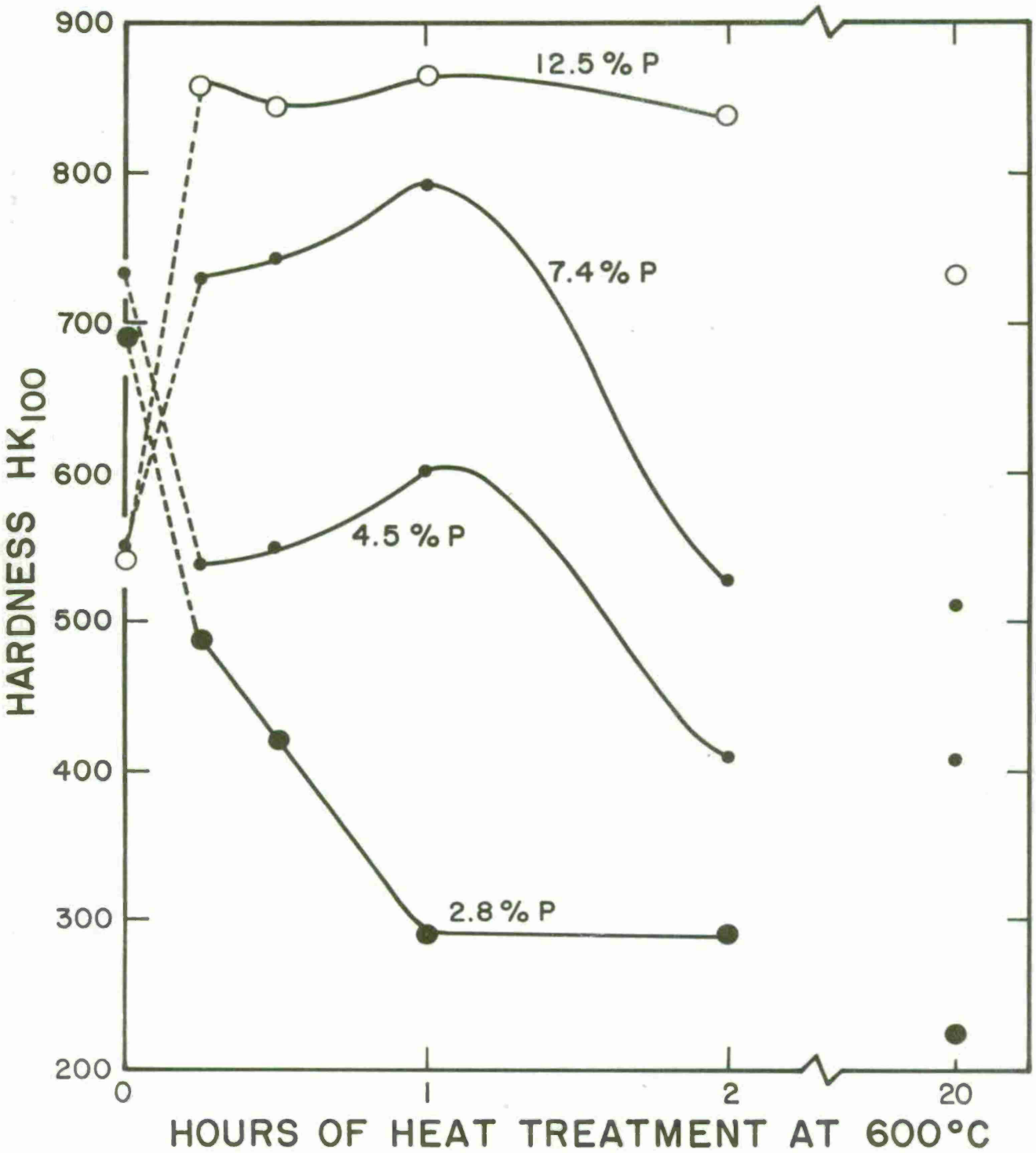


FIGURE 5 EFFECT OF DURATION OF HEAT TREATMENT AT 600°C ON HARDNESS

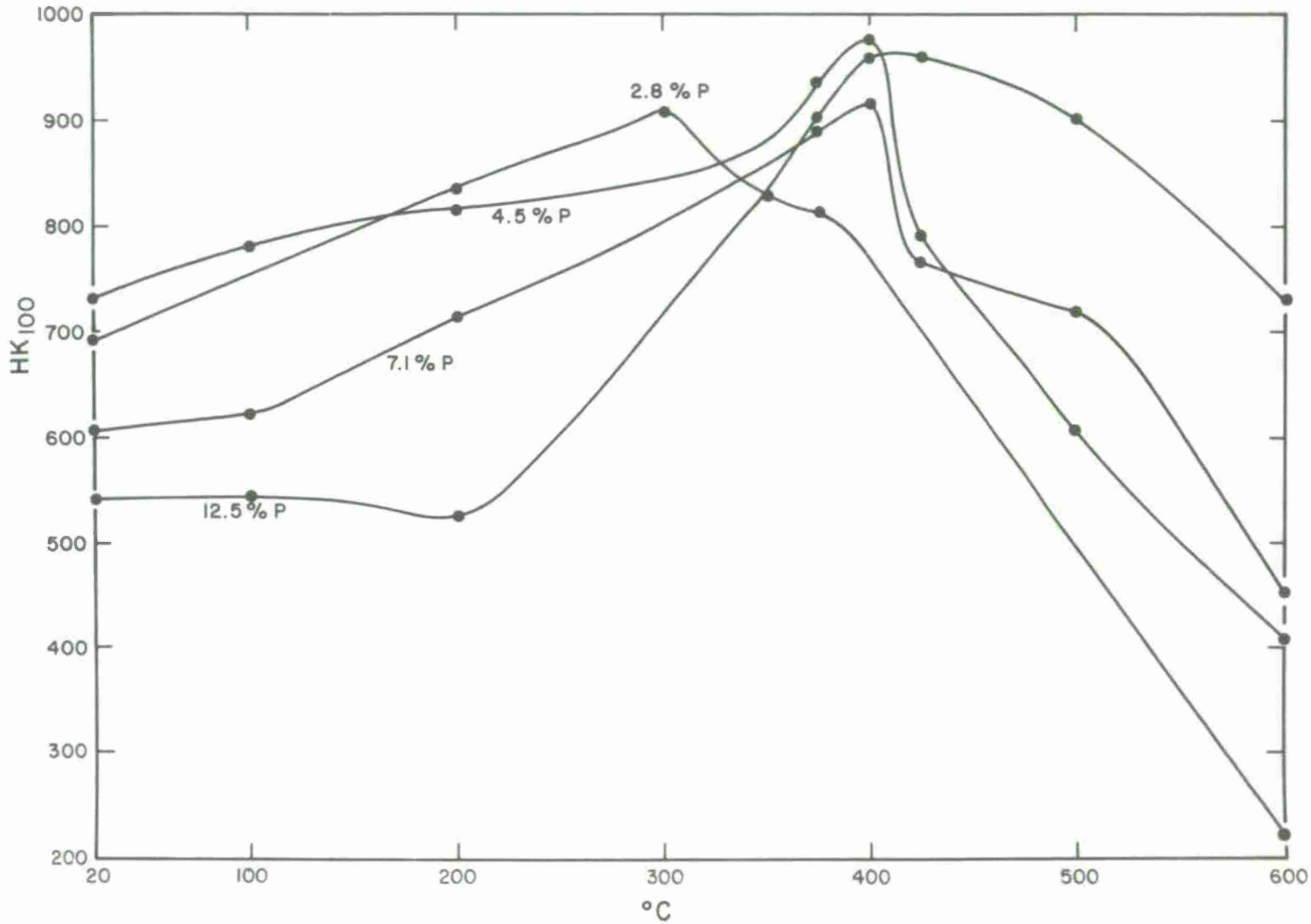


FIGURE 6

HARDNESS vs. TEMPERATURE OF HEAT TREATMENT
24 Hours at 100°C and 200°C
20 Hours at 300°C - 600°C

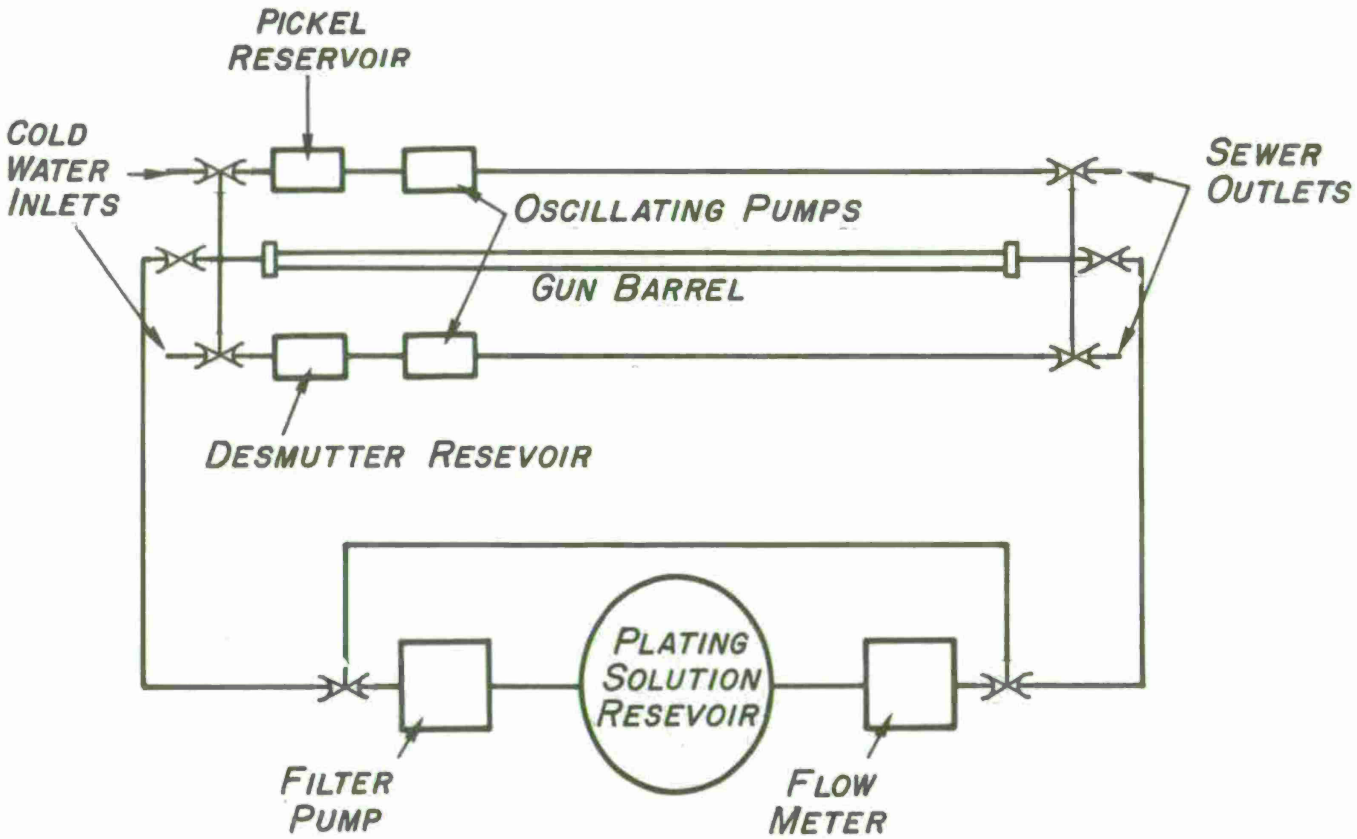


FIGURE 7 DIAGRAM OF EQUIPMENT FOR PLATING TUBE BORES

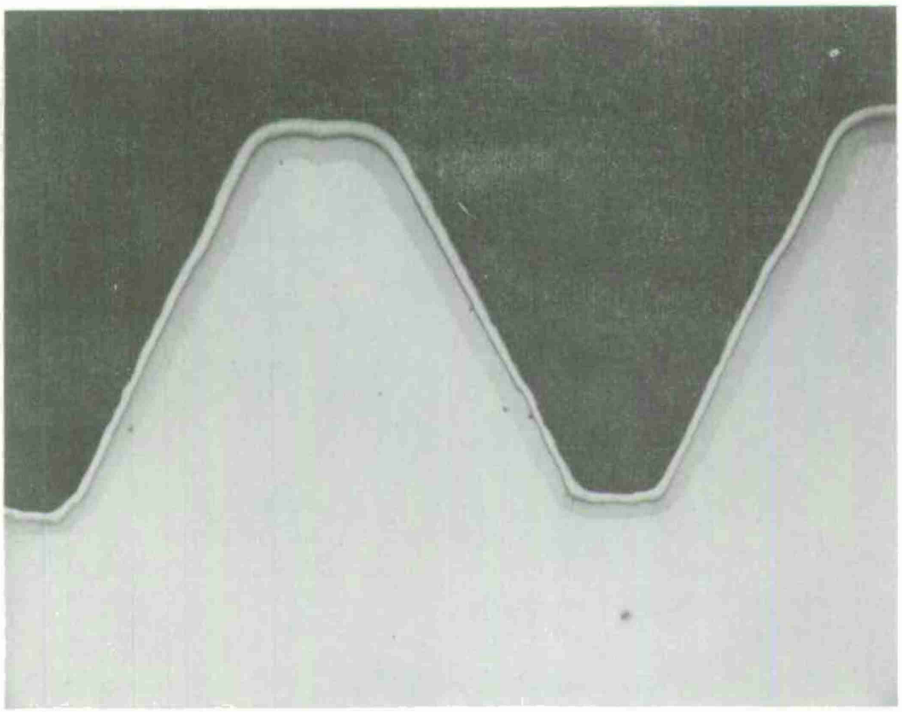


FIGURE 8 PHOTOMICROGRAPH OF CROSS SECTION OF BRASS BOLT PLATED WITH ELECTROLESS NICKEL IN BRENNER BATH WITHOUT AGITATION AT 0.6 MIL/HR. OVERPLATED WITH NICKEL. 90X PEAK TO VALLEY THICKNESS RATIO IS 2.

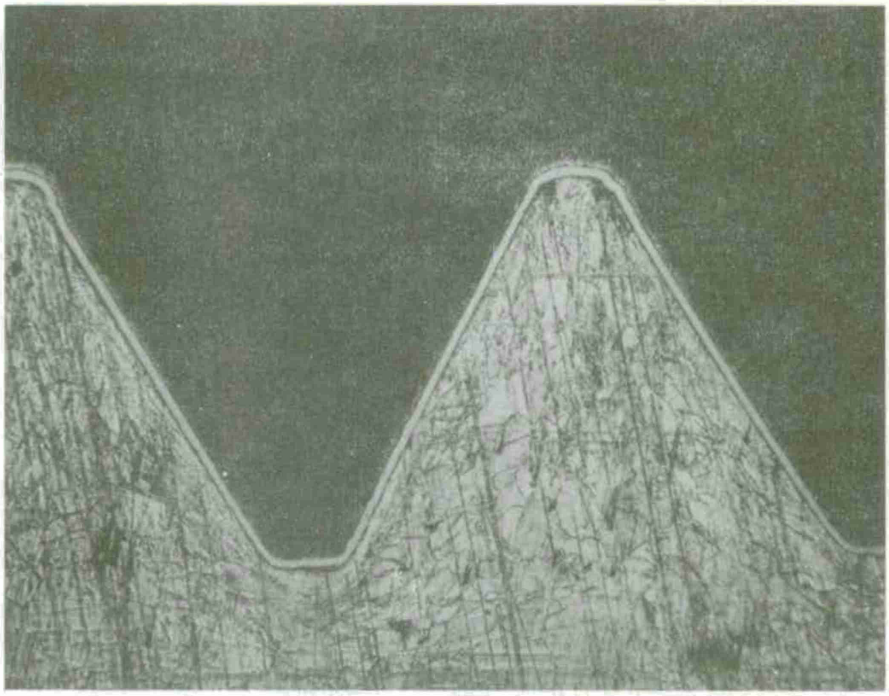


FIGURE 9 PHOTOMICROGRAPH OF CROSS SECTION OF BRASS BOLT PLATED WITH ELECTROLESS NICKEL IN BATH A WITHOUT AGITATION AT 0.2 MIL/HR. OVERPLATED WITH NICKEL. 90X
PEAK TO VALLEY THICKNESS RATIO IS 1.2

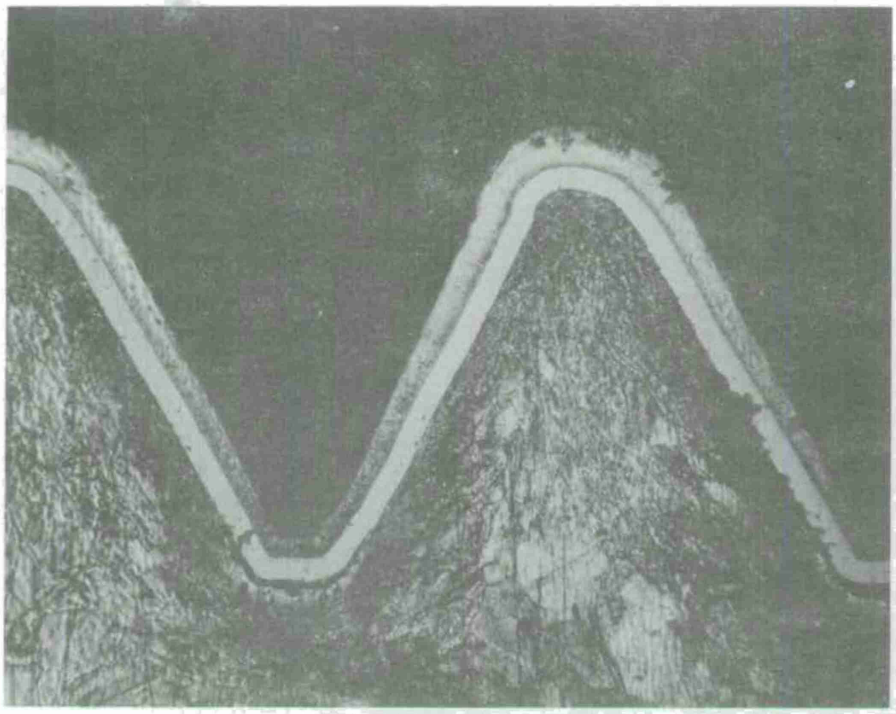


FIGURE 10 PHOTOMICROGRAPH OF CROSS SECTION OF BRASS BOLT PLATED WITH ELECTROLESS NICKEL IN BATH A WITH AGITATION AT 0.6 MIL/HR. OVERPLATED WITH NICKEL. 90X
PEAK TO VALLEY THICKNESS RATIO IS 1.01

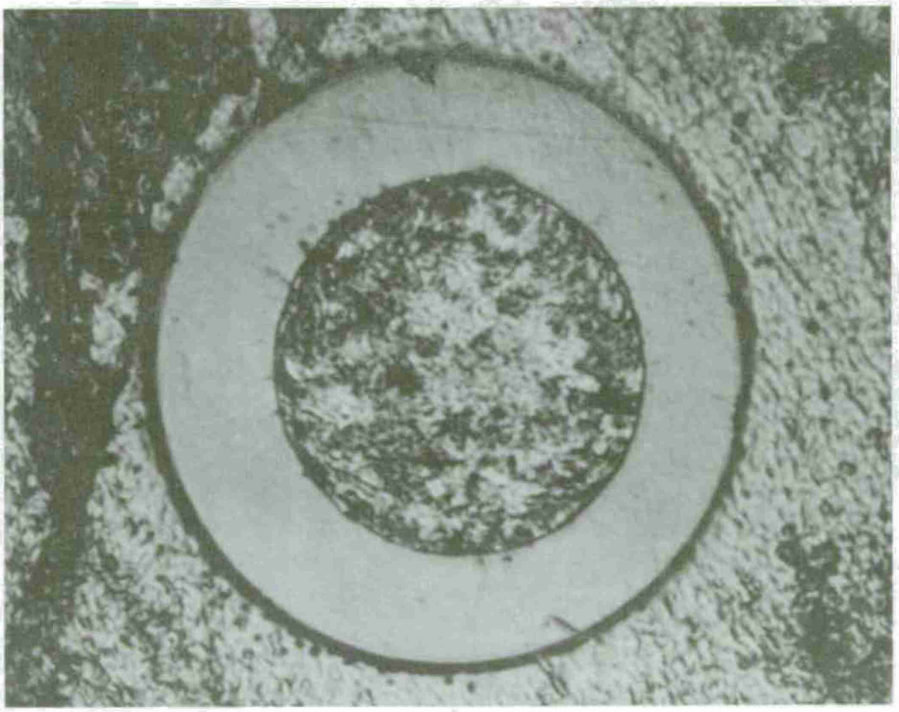


FIGURE 11 PHOTOMICROGRAPH OF CROSS SECTION OF 4 MIL COPPER WIRE PLATED WITH ELECTROLESS NICKEL IN BATH A WITH AGITATION AT 0.6 MIL/HR. OVERPLATED WITH NICKEL. 470X
MAXIMUM THICKNESS RATIO IS 1.25

TABLE I

OPERATING CONDITIONS FOR ELECTROLESS NICKEL DEPOSITS

Deposit No.	Type of Solution	pH	Temp. °C	Deposition Time Hours	Deposition Rate* mil/hr	Phosphorus Content of Deposit Per Cent	Page Reference
1	Brenner	6.6-4.2	96		0.65		3, 6
2	"	4.5-4.2	96				3, 6
3	"	4.5-4.2	96				3, 6
4	"	4.5-4.2	96		0.6 M		3, 6
5	"	4.5-4.2	96		0.75-0.51		3, 6
6	"	4.5-4.2	96				3, 6
7	"	4.5-4.2	96			11.1	3, 6
8	"	6.6-4.3	96	6	0.95-0.63		-
13	"	6.6-4.5	95	5	0.5 M	7.1	5
14	"	4.5-4.2	96	6	0.78-0.45	10.1	5
15	"	6.6-5.0	96	5	0.8 M	7.1	-
16	"	6.6-5.5	98	6		4.5	3
18	"	6.6-4.2		4-1/2	0.6 M	9.4	-
19	"	6.6-4.5	96	5-1/2	0.5 M	8.7	6, 8
20	"	6.6-4.4	50	71	0.03 M	12.5	5, 8
21	"	6.6-4.3	70	21	0.1 M	11.1	5, 8
22	"	6.6-4.4	60	44	0.06 M	11.9	5, 8
23	"	6.6-4.3	80	9-1/2	0.2 M	10.0	5, 8
24	"	5.6-4.5	96	7-1/2	0.5 M	9.4	3
27	"	6.6	96	4			-
29	Bath II	6.0	90	3	0.53	9.6	3
34	Bath I	4.6	85	7	0.54	6.8	3
35	"	4.6	85	6	0.52		3
36	"	4.6	85	9	0.54	7.2	3
37	"	5.2	87	2	0.78		3
38	Brenner	4.5	95	6	0.36	9.7	3
39	"	4.0	95	9	0.22	11.4	3
40	"	6.6-3.8	50	136	0.022	12.2	-
41	"	4.6	86	5	0.54		3
42	Bath I	4.7	86	4-1/2	0.57	7.4	3, 7
43	"	4.7	86	4	0.55	8.2	3, 7
44	"	4.6	86	5	0.54	8.0	3, 6
45	"	4.7	86	5-1/2	0.57	9.6	3, 6
46	"	4.8	86	3-1/4	0.65		3
47	"	4.5	86	5	0.50		3
48	"	4.5	85	5	0.47		3
49	"	4.5	86	5	0.39	10.3	3
50	"	4.8	86	5	0.43	10.0	3
52	"	4.7	86	9	0.54-0.29		4, 7
53	"	4.7	86	12-1/4	0.28	7.0	4, 7
54	"	4.7	86	12	0.27	7.2	4, 7
55	"	4.7	86	5-1/3	0.56	8.7	4, 7
56	"	4.7	86	5	0.60	10.1	4, 7
57	Bath II	5.8	90	4	0.5	12.8	4
58	"	5.8	90	4	0.37		4
59	"	6.1	90	3	0.36	12.1	4
60	"	5.8	90	4	0.55	12.6	-
61	"	5.8	90		0.33		-
62	Sulfamate	6.7-3.5	90	5	0.48	8.4	-
63	"	5-3.5	95	5-1/4	0.45		-
64	"	6-3.9	95	6	0.48		-
65	"	4-3.7	95	6	0.32		-
66	"	6.7-4.2	94	6	0.4		-
71	Bath III	5.8	90	4	0.54	12.1	-
80	Alkaline Sulfamate	9.5	75		0.5	6.5	8
81	"	9.5	80		0.5	5.5	8
82	"	9.5	90		0.67	5.2	8
86	Brenner Modified	6.0-6.6	95	5	0.25	2.8	-
88	Brenner Modified	6.0	95	5	0.2	3.7	-

* - Micrometer measurements are indicated by an M. Other thickness values were determined from weight and area measurements.

TABLE 2

HARDNESSES OF Ni-P ALLOYS
AS-PLATED AND AFTER HEAT TREATMENT

Deposit No.	Phosphorus %	As-Plated HK_{100}	8 Hr. 200°C HK_{100}	1/2 Hr. 400°C HK_{100}	1 Hr. 400°C HK_{100}	Type of Bath
60	12.6	524	520	-	855	II
57	12.6	518	523	-	845	II
20	12.5	536	508	961	-	Brenner
40	12.2	548	515	936	-	Brenner
71	12.1	509	521	840	766	III
22	11.9	561	491	957	-	Brenner
21	11.1	525	515	916	-	Brenner
7	11.1	554	560	883	-	Brenner
49	10.3	539	616	950	-	I
14	10.1	566	557	944	-	Brenner
56	10.1	544	639	948	-	I
23	10.0	512	491	957	-	Brenner
50	10.0	532	602	935	-	I
29	9.6	541	737	969	-	II
45	9.6	547	709	1001	-	I
18	9.4	547	-	936	-	Brenner
24	9.4	556	608	905	-	Brenner
19	8.7	584	628	890	893	Brenner
55	8.7	549	-	-	-	I
62	8.4	480	-	-	-	Sulfamate
43	8.2	540	702	934	-	I
44	8.0	546	717	953	-	I
42	7.4	551	731	969	-	I
36	7.2	539	767	940	-	I
54	7.2	576	735	847	-	I
13	7.1	602	720	921	-	Brenner
15	7.1	592	-	-	-	Brenner
53	7.0	569	762	858	-	I
34	6.8	611	736	852	-	I
80	6.5	679	-	-	-	Alkaline Sulfamate
81	5.5	660	-	-	-	Alkaline Sulfamate
82	5.2	624	-	-	-	Alkaline Sulfamate
16	4.5	732	811	911	923	Brenner
88	3.7	660	826[1]	-	829	Modified Brenner
86	2.8	692	835	-	812	Modified Brenner

[1] 48 hrs. at 200°C.

TABLE 3

EFFECT OF DURATION OF HEAT TREATMENT AT 100°C ON HARDNESS (HK_{100})

Deposit No.	Phosphorus %	As-Plated	4 hours	12 hours	1 day	2 days	3 days	9 days	Type of Bath
16	4.5	732	732	777	782	783	783	785	Brenner
34	6.8	611	-	-	610	-	-	602	I
13	7.1	602	-	-	623	-	631	671	Brenner
15	7.1	592	-	-	-	-	651	667	Brenner
14	10.1	566	-	-	-	-	563	565	Brenner
7	11.1	554	-	-	558	-	572	566	Brenner
20	12.5	536	-	-	542	-	-	580	Brenner

TABLE 4

EFFECT OF DURATION OF HEAT TREATMENT AT 200°C ON HARDNESS (HK_{100})

Deposit No.	Phosphorus %	As Plated	2 hours	4 hours	6 hours	8 hours	12 hours	1 day	2 days	3 days	6 days	9 days	Type of Bath
86	2.8	692	808	825	-	835	-	838	843	839	840	849	Modified Brenner
16	4.5	732	791	811	-	811	815	815	800	807	805	815	Brenner
34	6.8	611	684	734	-	736	748	739	734	731	737	766	"
13	7.1	602	-	-	-	720	-	716	-	-	-	724	Brenner
19	8.7	584	598	600	-	628	625	629	-	-	-	-	Brenner
71	12.1	509	521	478	512	521	524	524	530	540	556	564	"
40	12.2	548	519	515	-	515	517	520	532	541	544	543	Brenner
20	12.5	536	500	489	-	508	510	524	529	526	521	529	Brenner
57	12.6	518	512	475	525	523	524	519	523	525	532	561	"
60	12.6	524	513	461	517	520	521	525	527	522	542	556	"

TABLE 5

EFFECT OF DURATION OF HEAT TREATMENT AT 400°C ON HARDNESS (HK_{100})

Deposit No.	Phosphorus %	As-Plated	1/4 Hr.	1/2 Hr.	1 Hr.	2 Hrs.	20 Hrs.	Type of Bath
86	2.8	692	821	-	812	773	-	Modified Brenner
16	4.5	732	811	911	923	951	977	Brenner
34	6.8	611	782	852	915	957	967	"
13	7.1	602	-	921	-	-	916	Brenner
19	8.7	584	863	890	893	913	-	Brenner
71	12.1	509	845	827	890	766	-	"
20	12.5	536	959	961	953	961	960	Brenner
57	12.6	568	874	837	845	834	-	"
60	12.6	524	862	835	855	831	-	"

TABLE 6

EFFECT OF DURATION OF HEAT TREATMENT AT 600°C ON HARDNESS (HK_{100})

Deposit No.	Phosphorus %	As-Plated	1/4 Hr.	1/2 Hr.	1 Hr.	2 Hrs.	20 Hrs.	Type of Bath
86	2.8	692	-	-	288	290	-	Modified Brenner
16	4.5	732	539	550	602	410	408	Brenner
34	6.8	611	715	717	788	652	575	I
42	7.4	551	737	742	794	527	512	I
56	10.1	544	793	802	877	740	641	I
71	12.1	509	-	-	-	691	-	III
20	12.5	536	859	846	865	837	731	Brenner

TABLE 7

EFFECT OF HEAT TREATMENT - TEMPERATURE ON HARDNESS

Deposit No.	Phosphorus %	(24 hours at) 100°C	(24 hours at) 200°C	(20 hours at) 300°C	(20 hours at) 350°C	(20 hours at) 375°C	400°C	425°C	500°C	600°C	Time of Heat Treatment Hour	Type of Bath	As-Plated
86	2.8	-	-	831	848	-	812	-	-	288	1	Modified	692
		-	835	908	829	814	-	-	-	-	20	Brenner	
16	4.5	-	-	-	-	886	923	973	726	602	1	Brenner	732
		782	815	-	-	937	977	793	608	408	20	Brenner	-
34	6.8	-	-	-	-	785	915	1010	926	788	1	I	611
		-	-	-	-	943	967	877	838	575	20	I	-
13	7.1	-	-	-	-	758	-	958	843	-	1	Brenner	602
		623	716	-	-	890	916	765	721	452	20	Brenner	-
20	12.5	-	-	-	-	870	953	944	903	865	1	Brenner	536
		542	524	-	-	904	960	960	901	731	20	Brenner	-

TABLE 8

SPECIMENS PREPARED FOR BEAMS HIGH-SPEED ROTOR METHOD OF MEASURING ADHESION

	Substrate Material	Preplate Treatment	Electroless Nickel Bath
1.	1018 Steel 4140 Steel	pumice scrub, rinse ($Al(NO_3)_3$-HCl pickle, rinse.	I
2.	1018 Steel 4140 Steel	pumice scrub, rinse, 1 minute in 50% H_2SO_4 at 65°C, rinse, 2 minutes in lactic acid-peroxide solution at room temperature, rinse.	
3.	1018 Steel 4141 Steel	pumice scrub, rinse, 4 minutes in $Al(NO_3)_3$-HCl pickle at 42°C, rinse, 2 minutes in lactic acid-peroxide solution at room temperature, rinse.	
	$Al(NO_3)_3$-HCl pickle	4 minutes in solution of 400 g/l $Al(NO_3)_3$ and 400 ml/l conc. HCl.	
	Lactic acid-peroxide solution	15% lactic acid and 80 ml/l of 30% hydrogen peroxide.	

TABLE 9

ADHESION AFTER VARIOUS PRETREATMENTS

	Pretreatment	Adhesion: As-plated	Adhesion: After 1 Hour at 400°C
1.	As received.	VP	F
2.	Pumice scrub, rinse.	P	F
3.	Pumice scrub, rinse, 4 minutes in $Al(NO_3)_3$-HCl pickle, rinse.	VP	F
4.	Pumice scrub, rinse, 4 minutes in $Al(NO_3)_3$-HCl pickle at 42°C, rinse, lactic acid-peroxide solution, rinse.	F	G
5.	Pumice scrub, rinse, 4 minutes in $Al(NO_3)_3$-HCl pickle at room temperature, rinse, lactic acid-peroxide solution, rinse.	F	G
6.	$Al(NO_3)_3$-HCl pickle, rinse, lactic acid-peroxide solution, rinse.	F	G
7.	1 minute in 50% H_2SO_4 at 65°C, rinse, lactic acid-peroxide solution, rinse.	F	G
8.	5 minutes in 100 g/l sodium hypophosphite at 90°C, rinse.	VP	F
9.	3 minutes in $Al(NO_3)_3$-HCl pickle, rinse, 5 minutes in 100 g/l sodium hypophosphite at 90°C, rinse.	P	F
10.	1 minute in 40% H_2SO_4 at 65°C, rinse, 30 seconds in 1% H_2SO_4 + 0.1% HCl at room temperature, rinse.	F	F
11.	1 minute in 40% H_2SO_4 at 65°C, rinse, 1 minute in 50% HNO_3 at room temperature, rinse, 30 seconds in 1% H_2SO_4 + 0.1% HCl at room temperature, rinse.	P	G

$Al(NO_3)_3$-HCl pickle: 4 minutes in solution of 400 g/l $Al(NO_3)_3$ and 400 m/l con. HCl at 42°C.

TABLE 10

WEAR TESTS

Specimen	Number of Runs	Cycles Per mm	Type of Wheel	Weight Loss mg/1000 Cycles	Thickness Loss μm/1000 Cycles
Electroless nickel as-plated	5	5000	CS-10	9.1	0.42
	4	2500	CS-17	20.6	0.95
	1	5000	CS-17	14.6	0.67
Electroless nickel after 1 hr. at 400°C	5	5000	CS-10	7.6	0.35
	4	2500	CS-17	17.0	0.78
	1	5000	CS-17	13.5	0.62
Chromium	5	5000	CS-10	2.0	0.10
	2	2500	CS-17	8.4	0.43
Chromium after 1 hr. at 400°C	5	5000	CS-10	3.0	0.15

TABLE 11

COMPOSITION OF ELECTROLESS NICKEL-BORON BATHS

Bath	1	2	3	4	5
Nickel Chloride ($6H_2O$) g/l	30	30	30	-	30
Nickel Sulfate ($6H_2O$) g/l	-	-	-	20	-
Ethylenediamine (92%) ml/l	65	65	-	-	65
Glycolic Acid g/l	-	-	11.7	-	-
Citric Acid	-	-	-	10	-
Sodium Hydroxide g/l	40	40	-	-	40
Conc. Hydrochloric Acid ml/l	-	-	-	25	-
Ammonium Hydroxide to pH:	-	-	-	7	-
pH	13-14	13-14	5-6	-	13-14
Sodium Borohydride g/l	1.0	1.0	-	-	0.5
Dimethylamine Borane g/l	-	-	1.0	2.75	-
Sodium Cyanoborohydride g/l	-	-	-	-	0.15
Thallium Nitrate mg/l	7.0	100	-	-	-
Lead Acetate mg/l	-	-	20	-	-
Mercaptobenzothiozole mg/l	-	-	-	1.0	-
Temperature °C	80	80-95	65	70	90

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APPENDIX A

BANDED STRUCTURE OF ELECTROLESS NICKEL

TECHNICAL BRIEF

Banded Structure of Electroless Nickel

F. Ogburn and C. E. Johnson*

THE ETCHED CROSS SECTION of an electroless nickel (Ni-P) deposit generally is characterized by narrow or wide striations formed by variations in the degree of etching. These are usually attributed to variations in the phosphorus content of the deposit.[1] The evidence cited,[2] however, is meager and is based on appearance after treatment at 700°C for 1 hr and on potential variations during attack by red fuming nitric acid. Some of the heat-treated deposits show striations caused by variations of the population of dark particles, which were presumed to be Ni_3P precipitated during the heat treatment. There is no reason to doubt this explanation of the striations, but it would be more satisfying to have more direct evidence. Such evidence is given here.

Figure 1 is a photomicrograph of the etched cross section of an electroless nickel deposit, as plated, of the Ni-P type having wide striations. The 150 μm thick deposit was obtained at 96°C from an acid bath containing hydroxyacetic acid, similar to the original formulation of Brenner and Riddell.[3] The etching solution was 1 part nitric acid and 3 parts acetic acid. The Knoop diamond indentations were used as index marks for the electron probe analyses. Figure 2 is a photomicrograph of the same area with an electron probe trace of the phosphorus content superimposed. (Note the Knoop diamond indentations visible in Fig. 2.) Each dot in the row across the center indicates the location of a measurement by the electron probe. The beam size is actually about 0.5 μm in diameter and the measured x-rays are emitted from an area two or three times that diameter. The curve made up of dots on the upper part of the micrograph is a plot of the phosphorus content. A linear scale for the phosphorus content is on the ordinate with the maximum concentration on the curve at about 8 wt per cent. Zero per cent level is indicated by the row of dots in the lower left corner.

Comparison of the two figures indicates a reasonable inverse correlation between phosphorus content and the degree of etching.

More precise measurements were made on either side of the lower tips of the four indentations. From left to right, the measurements at each location are as follows:

Location	Wt Per Cent Ni	Wt Per Cent P
1	92.4	6.6
2	92.1	7.1
3	92.8	7.8
4	93.8	7.0
5	93.0	7.6
6	94.1	6.7
7	93.3	7.3
8	93.0	7.5

*Metallurgy Division, National Bureau of Standards, Washington, D.C. 20234.

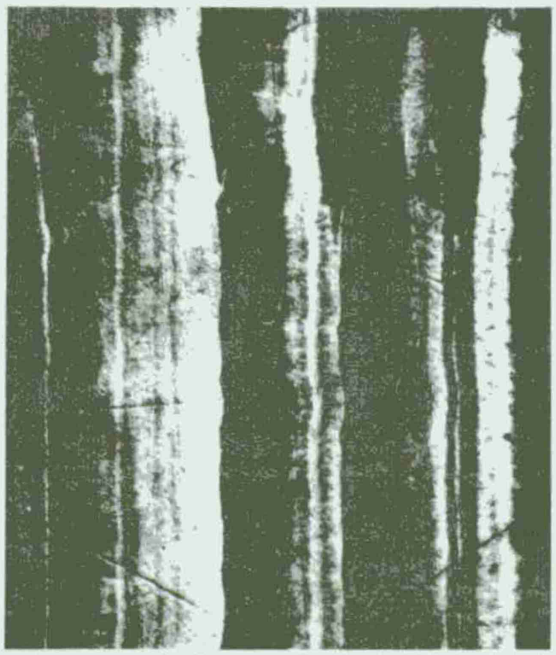

Fig. 1. Photomicrograph of cross section of electroless nickel deposit. Knoop indentations were made for indexing purposes.

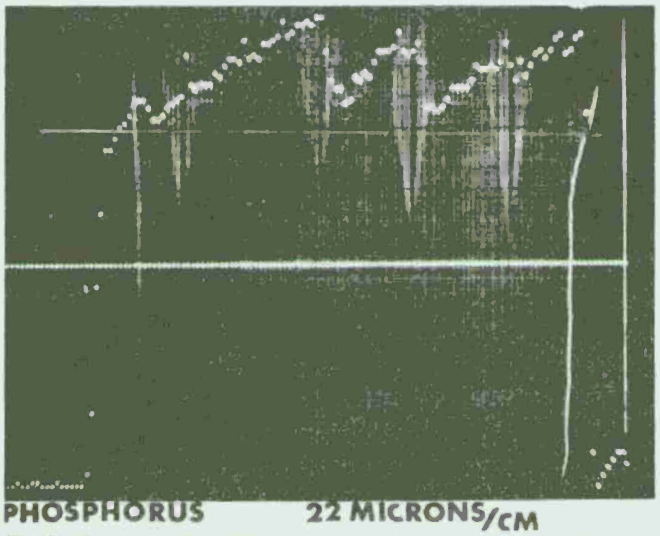

Fig. 2. Electron probe trace of phosphorus content across cross section of electroless nickel deposit. Zero per cent phosphorus is indicated by white dots in lower left corner. Maximum value is about 8 wt per cent phosphorus. Row of dots across center indicates position of each measurement.

Each of these values for phosphorus had, before rounding, a standard deviation of 0.7 per cent of the phosphorus concentration. Comparing these data with Fig. 1 shows again the inverse relation of phosphorus content with depth of etching.

Supporting evidence was also obtained from hardness measurements within a "white" band and an adjacent "dark" band on another portion of the same specimen which had been given only a light etch. The KH_{200} values were 483 and 526 respectively, the softer material being the more resistant to etching and having the greater phosphorus content. This is consistent with hardness measurements made on similar deposits of differing phosphorus content. Decreasing phosphorus corresponded with increasing hardness.

The relation between phosphorus content and etching rate of the as-plated alloy suggests a possible means of estimating the phosphorus.

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EFFECTS OF ELECTROLESS NICKEL PROCESS VARIABLES ON QUALITY REQUIREMENTS, by Fielding Ogburn and Christian E. Johnson - National Bureau of Standards

Report R-CR-76-032 Jun 76, 54 p. incl. illus., and tables (MIPR A1-2-65509-M2-M9, AMS Code 3297.06.7124) Unclassified Report.

The project objective was to determine the effects of production procedures on the characteristics of electroless nickel coatings. Deposition rate, phosphorus content, hardness, appearance, and metal distribution are reported for deposits from several hypophosphite type electroless nickel baths, both proprietary and non-proprietary. The baths were operated under a variety of conditions with variations of composition.

(Cont.) over

1. Autocatalytic nickel
2. Electroless nickel
3. Electroless plating
4. Nickel-phosphorus alloy

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