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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

ABSTRACT

Deposition rate, phosphorus content, hardness, appearance, and metal distribution are reported for deposits from two acid, hypophosphite type electroless nickel baths, one proprietary and one non-proprietary. The baths were operated under a variety of conditions with variations of composition. Extensive data is given on the relation of deposit hardness to phosphorus content and to heat treatment at 100, 200, and 400°C.

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 a non-proprietary acid bath and one proprietary bath. 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 is 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.

One proprietary solution was also used. This is not identified in this report, but is designated as bath A. Except as otherwise indicated, this was operated in accordance with the vendor's instructions.

Plating Cell

The basic plating cell was a glass cylinder of perhaps 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 approx-
imately 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 is summarized in Tables 1 and 2. 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 de-
posit. Additions were made continuously to the Brenner solution to main-
tain 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.

The proprietary bath was maintained as recommended by the vendor with
continuous addition of replenishment solutions and continual pH adjustment
with ammonium hydroxide. There were two replenishment solutions: Part
B containing the hypophosphite and Part C containing nickel and stabi-
lizers.

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.

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

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.

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

46, 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.

Deposit	Time hr	Final Nickel Concentration (oz/gal)
46	3-1/4	0.88
47	5	0.82
48	5	0.88

Deposits 49 and 50 were obtained from the same bath as #48 with the nickel concentration maintained at 0.88 oz/gal 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 content of the deposits.

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 A 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 A 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.

In the literature [2] 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.

Specimen	Temperature	Plating Time	Weight of Deposit	Rate of Deposition*	
20	50°C	71 hr	2.051 g	0.71 μm g/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

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 A, 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 gotten 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.

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 striated appearance. This is

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*Density assumed to be 7.85 [3].

associated with variations in the phosphorus content and has been mention-
ed 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 submitted to Plating for publication as a technical note.

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 [6] 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 phos-
phorus 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 was 11.1% P.

The effect of accumulation of phosphite in bath A 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.

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
A and were 7.4 and 8.2% P respectively. Another new bath A was operated
9 hours in the normal manner but without addition of the Part B replen-
ishment solution (Deposit 52). At the end of the 9 hours, chemical
analysis indicated 2.1 fl. oz/gal of the Part B reducing solution. The
normal concentration is about 9 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 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 5 hours of operation with normal Part B replenishment, but after bringing the reducing 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 A:			
42	4-1/2	7.6	9
43	4	8.2	9
Another New Bath A 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.

Hardness Measurement

All hardness measurements were made with a Knoop indenter using a Wilson 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 most 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 preceeding 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.

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 tested 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 (Figure 1) 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. The hardness data of Table 2 is all for a load of 100 g. Most of the data was obtained using a load of 100 g, but some of it as indicated in the table was obtained at a greater load and converted to that for the 100 g load.

Hardness Data

The hardness data is summarized in Table 2. It includes hardness of as plated deposits and of deposits which had been treated at 100, 200, and 400°C for various times.

The hardness of electroless nickel, as-plated, without heat treatment, usually does not show much variation. The Electroplating Engineering

Handbook [6] gives the range as 500±50 DPH. Several investigators have recognized a relationship between the hardness of the deposit and its phosphorus content. Graham et al [4] reported that for a specific well controlled alkaline bath, the hardness of the deposits decreased from 560 to 530 KHN as the phosphorus content increased from about 4.5% to 9.5%. Randin and Hinterman [5] using an acid solution show a pronounced minimum in the hardness at about 6.3% phosphorus. Their relationship was quite different from that of Graham et al.

The data for as-plated deposits given in Table 2 is summarized in Figure 2 where the hardness is plotted against the phosphorus content. These data include deposits from bath A and the Brenner bath, all of which were operated at more than one composition and several different operating conditions. Thus these data represent a variety of electroless nickel deposits. The scatter of the data is, in part, due to the nonuniformity of each deposit and to imprecision of measurement. Another very likely cause of the scatter is that some feature or features of electroless nickel other than phosphorus content, influences the hardness.

It appears that for phosphorus concentrations above 7%, variations of phosphorus are of little practical consequence to hardness. Below 7%, the indication is that the phosphorus has much more to do with the hardness. More data, however, is needed for this phosphorus range.

Heat treatment at 100°C has some effect on hardness as shown by Figure 3, but this is probably of no practical significance. The changes are small and slow. It is possible that changes would be significantly greater over periods of months or years. It is interesting to note that the initial rate of change of hardness with time is related to the phosphorus content.

A number of specimens were heat treated at 200°C because such a treatment is often used for embrittlement relief. The hardness effects of heating at 200°C are summarized in Figure 4, which indicates that the hardness may either increase or decrease. In general, the deposits get harder, but those deposits from the Brenner bath with more than 9.8% P become a little bit softer. Figure 4 is for an 8 hour treatment. Figure 5 shows how the hardness varies with time. For low phosphorus content, 4 - 7% P, the heat treatment is essentially complete within four hours. At 8.7% P it was complete within eight hours. For high phosphorus deposits from the Brenner bath, the hardness drops during approximately the first four hours and then returns to approximately its original hardness during the balance of the first 24 hours.

The deposits from the proprietary solution increased in hardness more than those from the Brenner solution.

It is generally recognized that maximum hardness of electroless nickel is obtained by heat treatment at 400°C. Figure 6 shows how the hardness changes with the time at 400°C. The rate of increase of hardness is quite rapid at first and then tapers off so that after 1 or 2 hours there is not much change. The hardness range for deposits heated to

400°C for 1/2 hour is 852 to 969 KH_{100}. The time needed to obtain the maximum hardness was not determined, but the data for 20 hours indicates that 2 hours is not enough, and the rate of change after 2 hours is quite small.

The final hardness does not appear to be closely related to phosphorus content, but the phosphorus appears to have an effect on the initial rate of hardness change.

A few specimens were heat treated at 375, 425, and 500°C in order to determine how critical the temperature is for maximum hardness. These data are plotted in Figure 7. They indicate that after 20 hours at 375°C, the hardness is not far below the maximum. At 425°C, the low phosphorus samples showed a markedly lower hardness and the high phosphorus deposit showed virtually no difference compared to the maximum.

These data are quite similar to those of Randin and Hinterman [5].

Thickness Uniformity

The Electroplating Engineering Handbook 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 A 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 replacement relative to deposition of nickel.

Figure 10 is of a bolt plated near the faster rate in bath A 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 A 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

Those coating characteristics which have been considered in this report are appearance, roughness, hardness, and thickness. These should be discussed in terms of the process control.

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 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 for two types of baths, of the data of Graham et al [4], and of that of Randin and Hinterman [5]; several generalizations can be made about the hardness of electroless nickel deposits.

1) For practical purposes, the as-plated hardness of electroless nickel phosphorus alloy is independent of the bath and operating conditions if the deposit is greater than 7-1/2% P. Below about 7% P, the hardness seems to be related to the phosphorus content and dependent on the particular process used.

2) Heat treatment at 200°C can increase the hardness by about 300 units, but it can also decrease the hardness by 30 units. What happens depends on the type of electroless nickel process and on the time of heat treatment. Three hours will probably not be long enough to attain maximum hardness for this temperature and 8 hours will be more than enough for practical purposes.

3) Maximum hardness is attained by heating at 400°C. For practical purposes 2 hours of heating is sufficient and 1 hour would usually suffice. The hardness obtained varies from deposit to deposit, but the variation appears to be less than 120 units out of about 925 KH_{100}.

If the deposits are heated above 400°C, the hardness will drop considerably for low phosphorus content and very much less for high phosphorus content. The difference is very evident after 20 hours at 425°C.

Tensile strength and ductility are important to applications of electroless nickel. These properties were measured by Graham et al [4] for deposits with 4-3/4 - 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 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. One recommended procedure is to plate a coupon simultaneously with plating of the work piece. Appropriate weight and area measurements of the deposit on the coupon would provide a reasonably good thickness estimate.

Uniformity of coating thickness cannot be assumed. A 2 to 1 variation is possible. Agitation can even out the metal distribution and it can make matters worse; though, in general, it is probably helpful.

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TABLE 1

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		2
2	"	4.5-4.2	96				2
3	"	4.5-4.2	96				2
4	"	4.5-4.2	96		0.6 M		2
5	"	4.5-4.2	96	6	0.75-0.51		2
6	"	4.5-4.2	96				2
7	"	4.5-4.2	96			11.1	5
8	"	6.6-4.3	96	6	0.95-0.63		-
13	"	6.6-4.5	95	5	0.5 M	7.1	4
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	96	6		4.5	2
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	5, 7
20	"	6.6-4.4	50	71	0.03 M	12.5	4, 7
21	"	6.6-4.3	70	21	0.1 M	11.1	4, 7
22	"	6.6-4.4	60	44	0.06 M	11.9	4, 7
23	"	6.6-4.3	80	9-1/2	0.2 M	10.0	4, 7
24	"	5.6-4.5	96	7-1/2	0.5 M	9.4	2
27	"	6.6-	96	4			-
34	Bath A	4.6	85	7	0.53	6.8	2
35	"	4.6	85	6	0.52		2
36	"	4.6	85	9	0.54	7.2	2
37	"	5.2	87	2	0.78		2
38	Brenner	4.5	95	6	0.36	9.7	2
39	"	4.0	95	9	0.22	11.4	2
40	"	6.6-3.8	50	136	0.022		-
41	"	4.6	86	5	0.54		2
42	Bath A	4.7	86	4-1/2	0.57	7.4	2
43	"	4.7	86	4	0.55	8.2	2
44	"	4.6	86	5	0.54	8.0	2

TABLE 1 (Continued)

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
45	Bath A	4.7	86	5-1/2	0.57	9.6	2
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		3, 5
53	"	4.7	86	12-1/4	0.28	7.0	3, 6
54	"	4.7	86	12	0.27	7.2	3, 6
55	"	4.7	86	5-1/3	0.56	8.7	3, 6
56	"	4.7	86	5	0.60	10.1	3, 6

* - Micrometer measurements are indicated by an M. Other thickness values were determined from weight and area measurements.
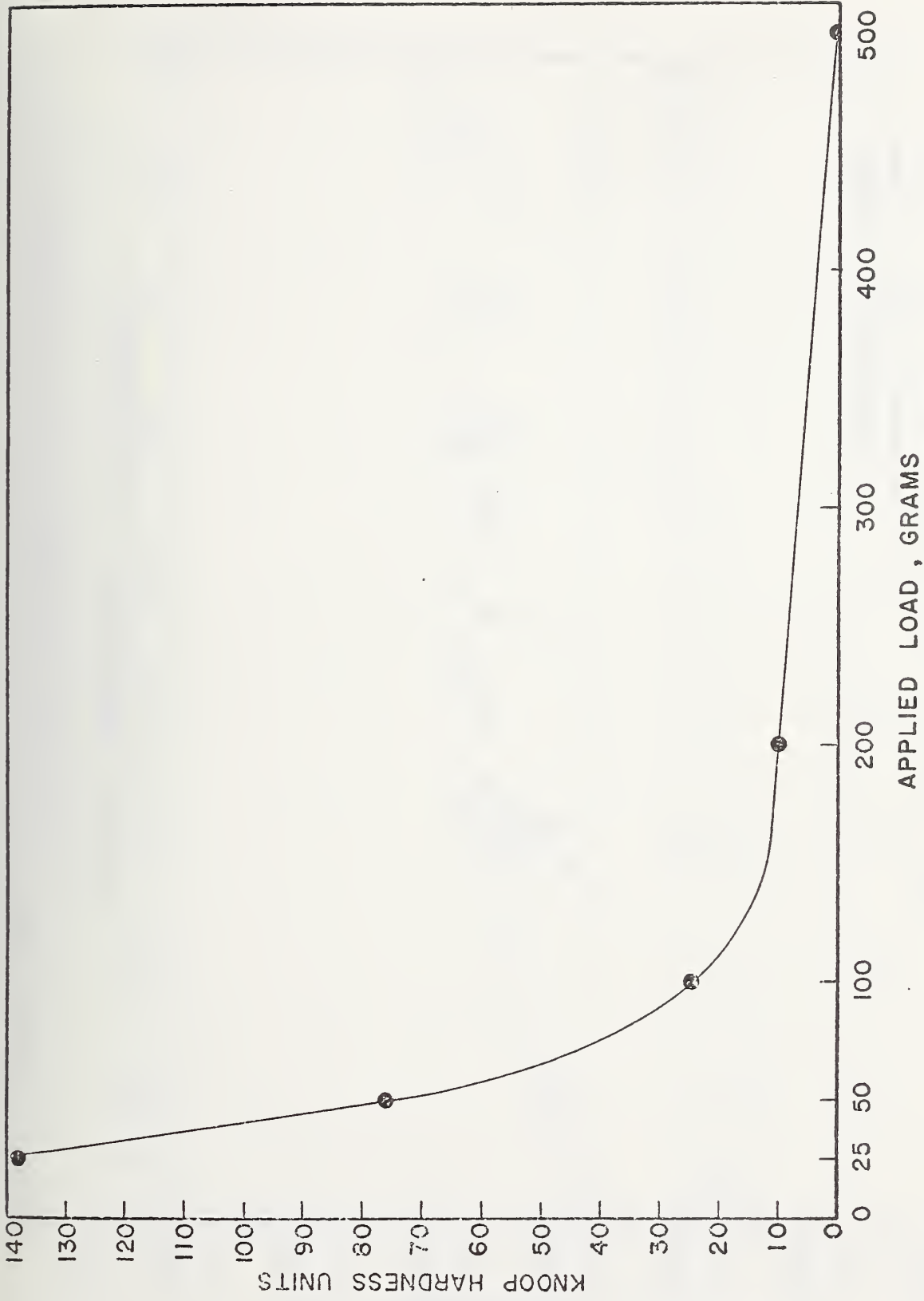
Figure 1 - HARDNESS CONVERSION CURVE.
Used For Correcting Hardness Values When Changing From One Applied Load To Another
Without Making An Actual Measurement. Such As, Changing The Load From 500 g To
100 g; 25 Hardness Units Must Be Added To The Hardness Value Obtained at 500 g.
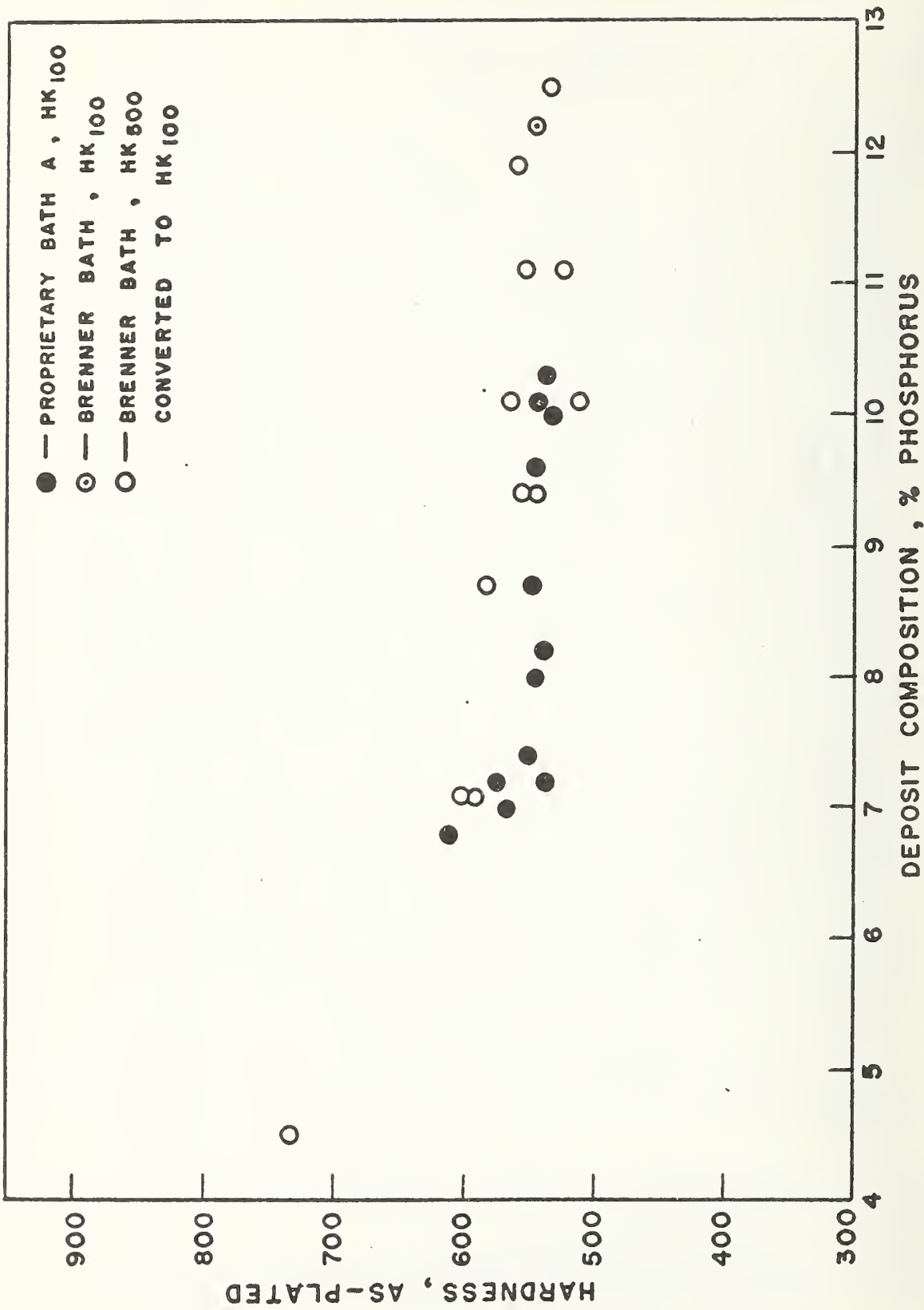
Figure 2 – AS-PLATED HARDNESS AS A FUNCTION OF PHOSPHORUS CONTENT IN THE DEPOSIT.
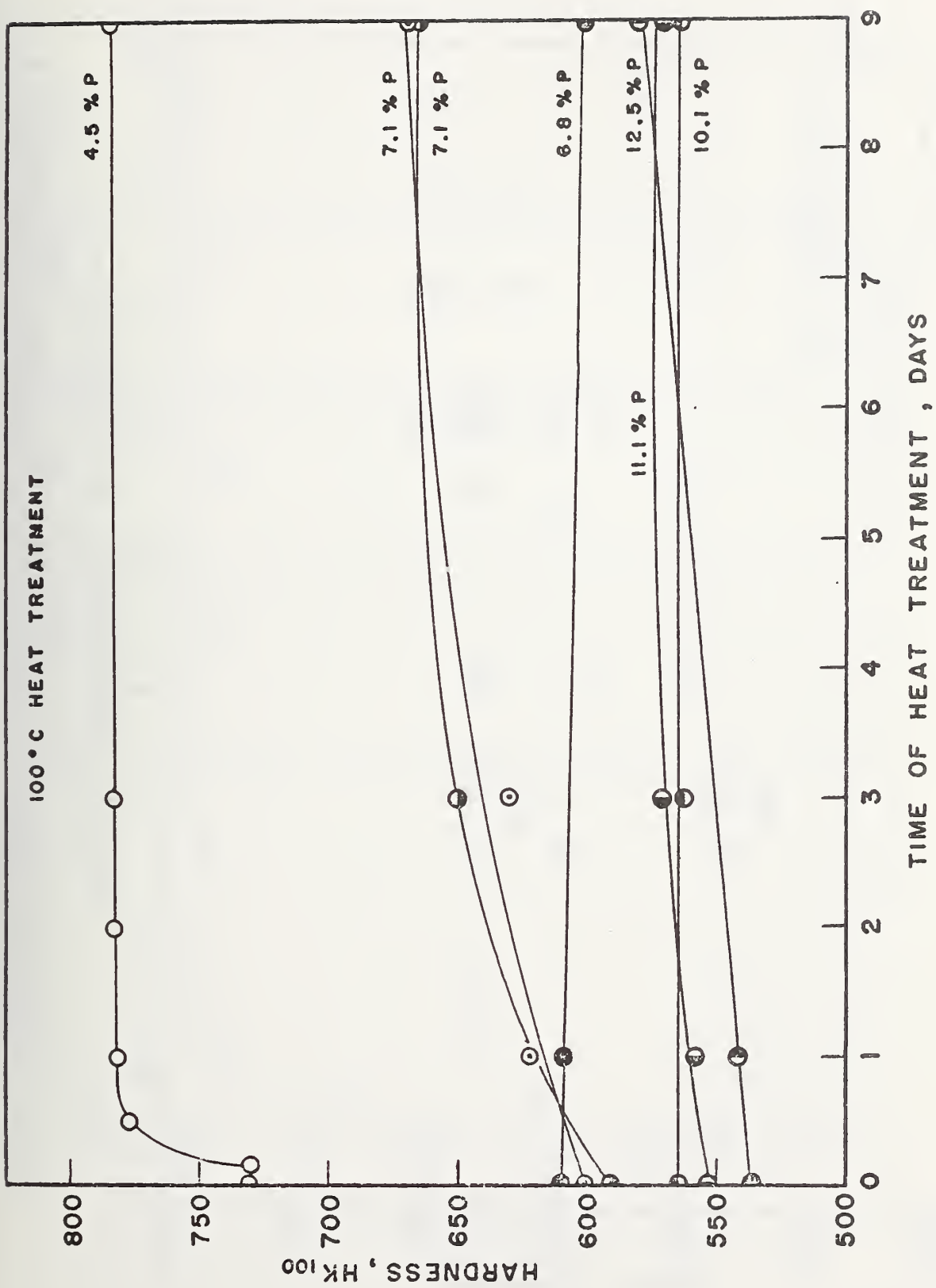
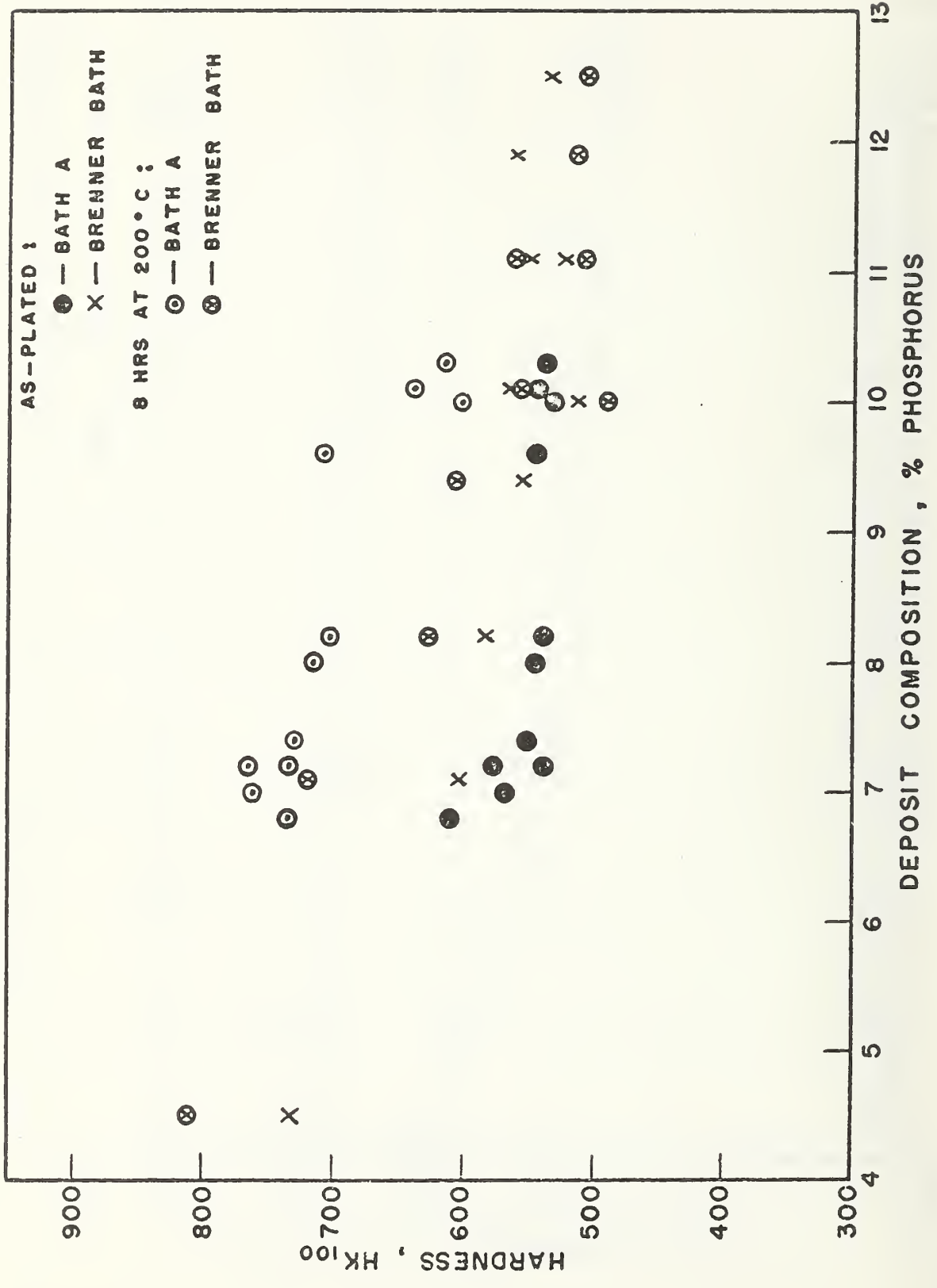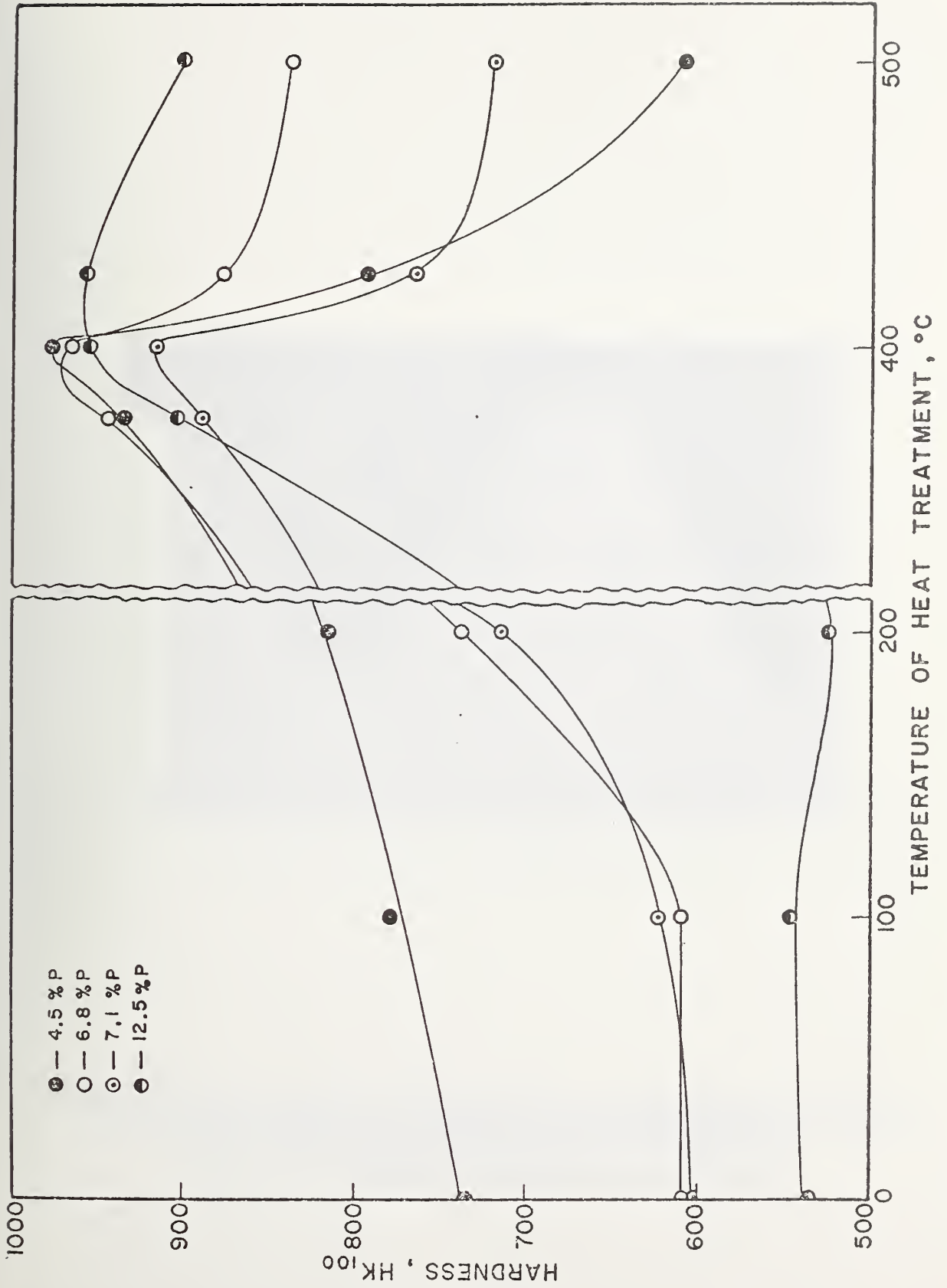Figure 3 – HARDNESS AS A FUNCTION OF TIME AT 100°C HEAT TREATMENT FOR VARIOUS PHOSPHORUS CONTENT DEPOSITS.

Figure 4 - HARDNESS AS A FUNCTION OF PHOSPHORUS CONTENT IN THE DEPOSIT AFTER 8 HOURS OF 200°C HEAT TREATMENT.
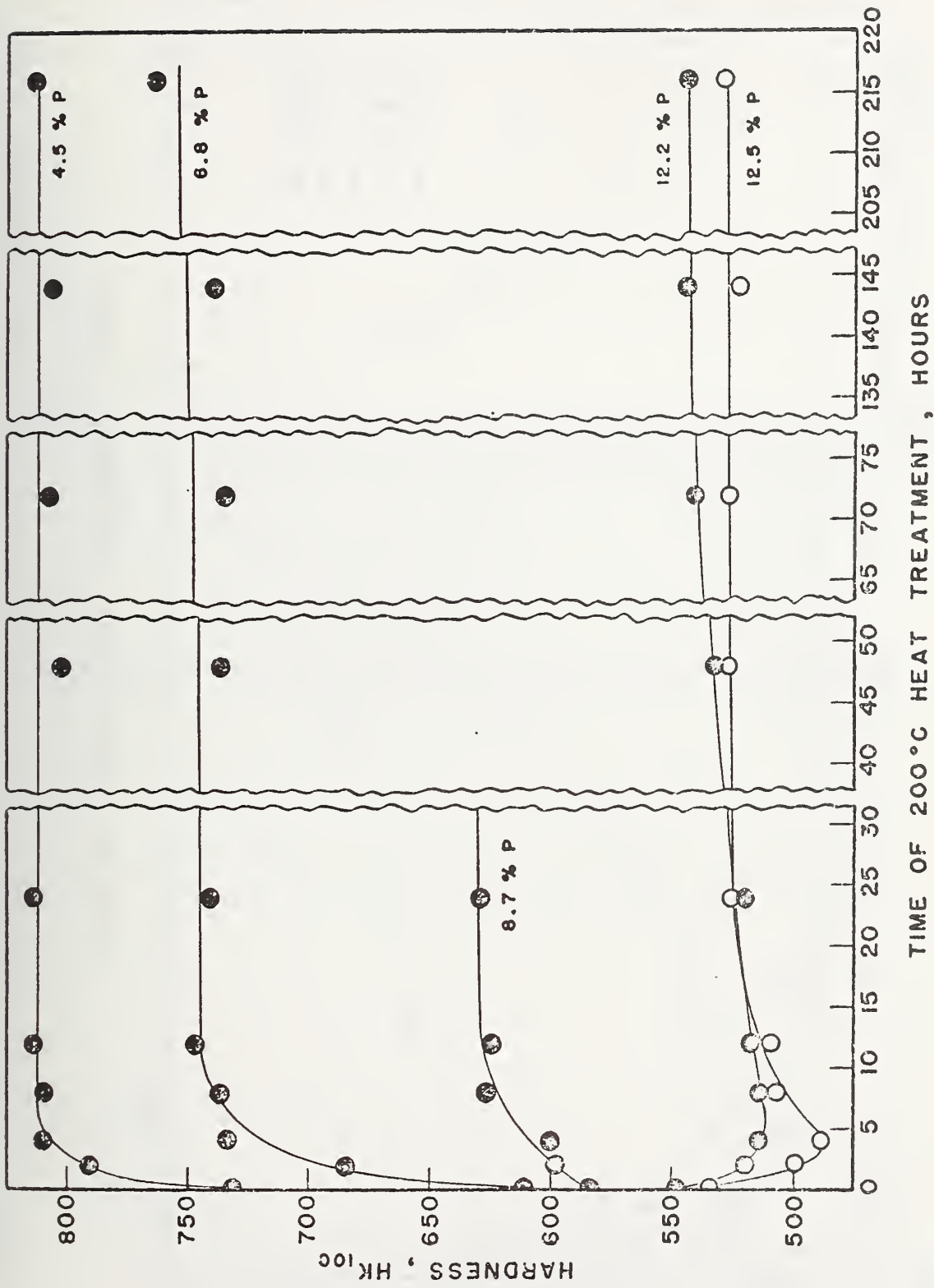
Figure 5 - HARDNESS AS A FUNCTION OF TIME AT 200°C HEAT TREATMENT FOR VARIOUS PHOSPHORUS CONTENT DEPOSITS.
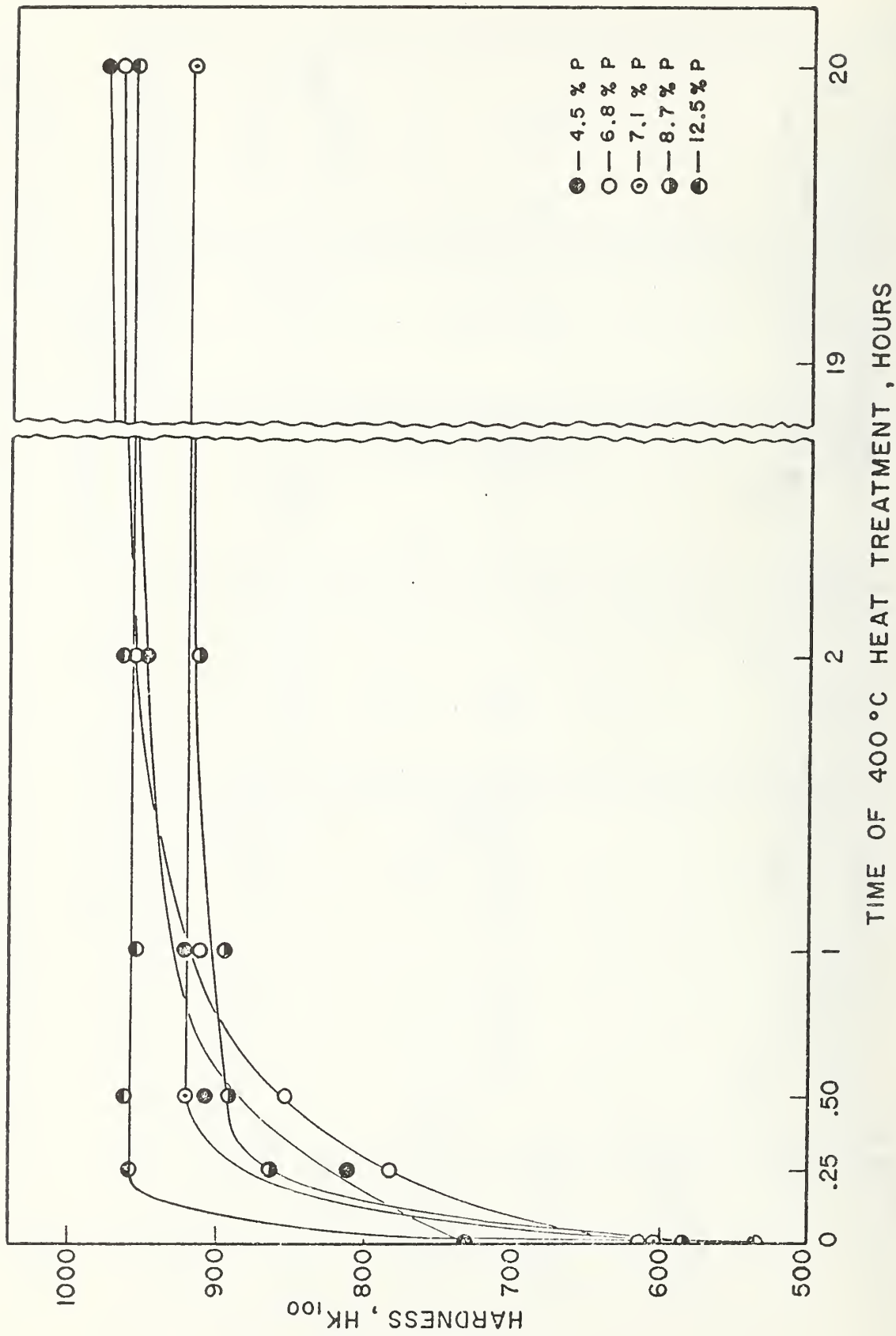
Figure 6 - HARDNESS AS A FUNCTION OF TIME AT 400°C HEAT TREATMENT FOR VARIOUS PHOSPHORUS CONTENT DEPOSITS.

Figure 7 - HARDNESS AS A FUNCTION OF 20 TO 24 HOURS OF HEAT TREATMENT AT DIFFERENT TEMPERATURES FOR VARIOUS PHOSPHORUS CONTENT DEPOSITS.
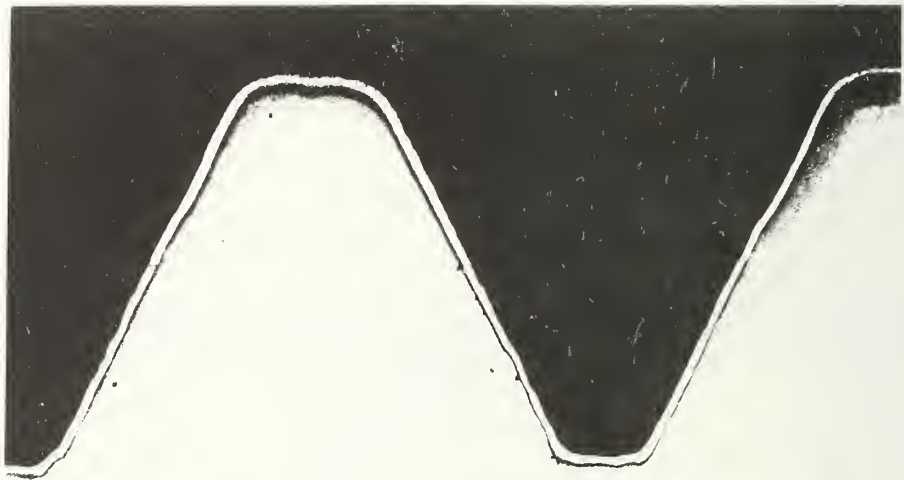
Figure 8 - Photomicrograph of cross section of brass bolt plated with
electroless nickel in Brenner bath without agitation at
0.6 mil/hr. Overplated with nickel. 90X
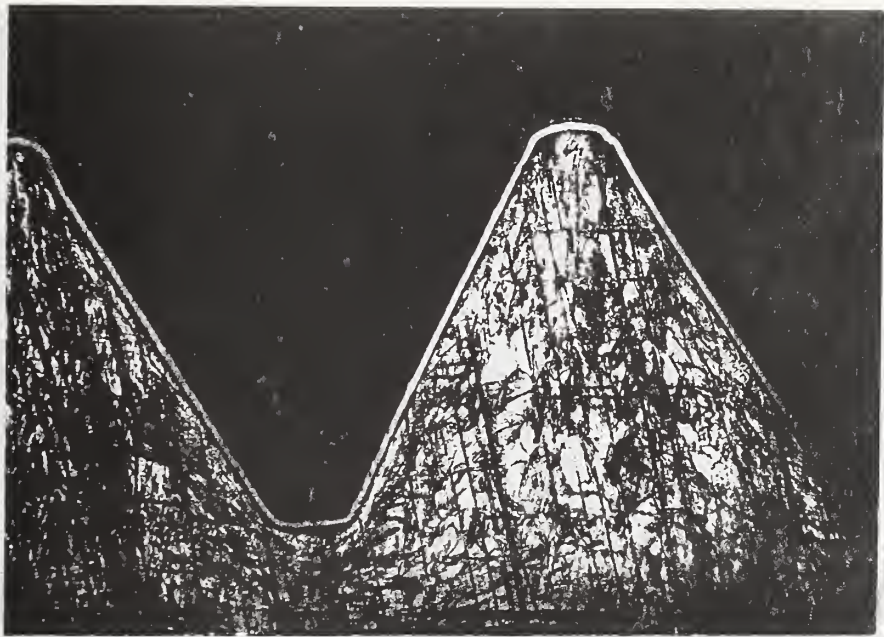Peak to valley thickness ratio is 2.

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
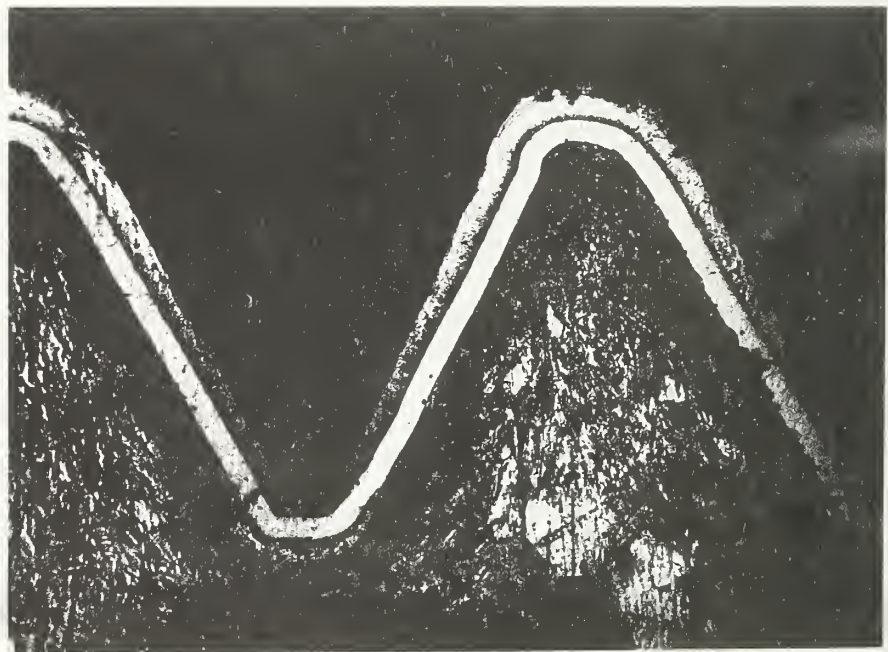Peak to valley thickness ratio is 1.2.

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
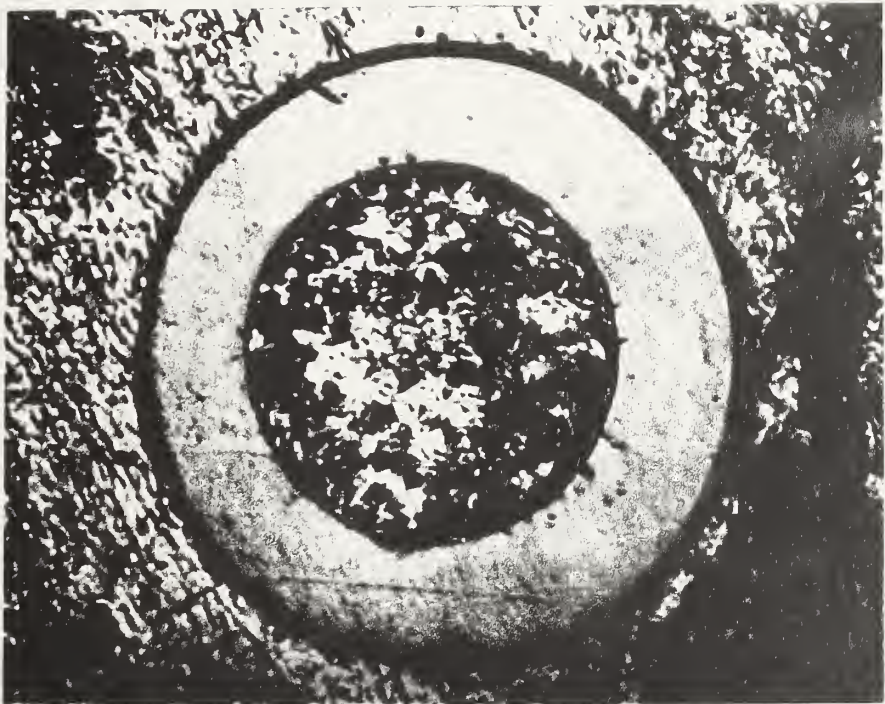Peak to valley thickness ratio is 1.01.

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.

APPENDIX A

TECHNICAL BRIEF

BANDED STRUCTURE OF ELECTROLESS NICKEL

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Washington, D.C. 20234

The etched cross section of an electroless nickel (Ni-P) deposit generally is characterized by narrow and/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 700C for 1 hour. Some of these 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. It was deposited 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 Figure 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 concen-
tration on the curve at about 8 wt.%. Zero percent level is
indicated by the row of dots in the lower left corner.

Comparison of the two figures indicates a reasonable in-
verse 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:

	Wt.%	
Location	Ni	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

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

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

This work was carried out as part of a project supported by the Weapons Laboratory - RIA, Rock Island Arsenal, Rock Island, Illinois.

References

[1] Electroplating Engineering Handbook, Third Edition, Edited by A. K. Graham, Van Nostrand Reinhold Co., New York, 1971, p. 498.

[2] A. W. Goldenstein, W. Nostoker, and F. Schossberger, Jr., Electrochem. Soc. 104, 104 (1957).

[3] A. Brenner and G. E. Riddell, Proc. Amer. Electroplaters' Soc. 34, 156 (1947).

Figures

Figure 1. Photomicrograph of cross section of electroless nickel deposit.

Knoop indentations were made for indexing purposes.

Figure 2. Electron probe trace of phosphorus content across cross section

of electroless nickel deposit. Zero percent phosphorus is

indicated by white dots in lower left corner. Maximum value

is about 8 wt.% phosphorus. Row of dots across center indi-

cates position of each measurement.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

Deposition rate, phosphorus content, hardness, appearance, and metal distribution are reported for deposits from two acid, hypophosphite type electroless nickel baths, one proprietary and one non-proprietary. The baths were operated under a variety of conditions with variations of composition. Extensive data is given on the relation of deposit hardness to phosphorus content and to heat treatment at 100, 200, and 400°C.

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