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Codeposition of Wear-Resistant Particles ~~of~~ with Chromium

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ABSTRACT

Efforts to include particles in deposits from standard chromium baths over a wide range of plating conditions were futile. Inclusion of particles was achieved only by adding any of a number of monovalent cations to the chromium bath such as Tl, Ce, Na, NH, Li. Under the plating conditions developed all particles that were added to the bath were included from a few tenths to 5 wt.% in chromium deposit without excessive loss of properties. Particles included were diamond, borides, carbides, nitrides, oxides, metals, graphite, and a sulfide. The more conductive materials were more easily included. A bath-life test using additives and particles was run for thousands of ampere-hours per liter of solution with good bath performance. Wear tests of deposits having included particles indicated improved wear-resistance. A caliber 0.30 tube was plated with chromium having included particles which had good particle distribution throughout the bore. Deposits of cadmium and zinc with included hard particles showed improvement in wear-resistance.

OBJECTIVE

The experiments described in this report were intended to improve the wear-resistance of deposited coatings, mainly chromium, by incorporating hard particles in the deposits and determining the wear-resistance and other properties of such coatings and to develop a practical bath and set of operating conditions whereby the inclusion of particles in chromium could be accomplished on a more or less production basis.

CODEPOSITION OF WEAR-RESISTANT PARTICLES WITH CHROMIUM

INTRODUCTION

A search of the literature revealed that electrodeposited composite coatings with a metal (usually nickel) matrix and dispersed particles have been used for wear-resistance, anti-friction, and dispersion hardening. The characteristics of the usual electrolytes for plating hard chromium, however, make the deposition of inclusions in chromium coatings difficult. The low efficiency of the baths results in copious evolution of hydrogen causing vigorous agitation of the solution at the cathode surface. The consequent slow rate of deposition further reduces the chance of retaining particles in the chromium deposit. Maximum hardness and current efficiency are primarily a function of electrolyte composition, bath temperature, and current density. It has already been determined[1] that higher current efficiency is obtained at lower chromic acid concentrations in the sulfate-catalyst bath. The surface concentration also affects efficiency with the optimum chromic acid-sulfuric acid ratio being in the range of 70 to 100 to 1. The build-up of trivalent chromium over 5 or 10 g/l in the bath likewise reduces efficiency because of increased resistance in the solution.

The hardness of the chromium deposits is fortunately greatest at lower concentrations of chromic acid, trivalent chromium and acid catalyst. Unfortunately, non-soluble, hard particles added to the bath could not be codeposited at these optimum conditions. The particles tried were smaller than 25 µm and consisted of oxides of aluminum and titanium, silicon carbide and later, diamond dust. A variation of the sulfate bath, the Bornhauser bath[1], containing sodium hydroxide, gives deposits which are quite dull and soft by hard chromium standards but did allow codeposition of particles.

Investigation has shown that soluble additives, both inorganic and organic, can enhance the hardness and wear resistance, as well as the brightness of chromium deposits[2]. The most effective of these additives was tried and, although it did slightly enhance the properties of the deposit, it did not promote the inclusion of particles.

Work done on the codeposition of particles in the copper sulfate bath[3], which, like the chromium bath, is highly acidic, showed that bath-soluble salts of monovalent cations permitted extensive codeposition of bath-insoluble particles. The most effective of these were thallium salts at a concentration of 5 to 10 g/l. The addition of thallium was tried in the hard chromium plating bath and resulted in the codeposition of hard particles in the chromium matrix. The wear resistance of some of these composite chromium coatings was substantially improved over the best of the standard bright, hard chromium deposits. Powdered metals were also codeposited with chromium with the possibility of forming chromium alloys by heat-treating the coatings. In nearly all cases, the codeposited particles amounted to less than five percent by weight of the chromium deposit. In cases where particle content of much more than 5% occurred, the properties of the chromium deposit were seriously degraded. Other types of particles tried included boron nitride, zirconium silicate, two sizes of aluminum oxide and fumed aluminum oxide and silica. Other monovalent cations, besides thallium, that were used included salts of cesium, lithium, sodium, and ammonia. All of the particles were included in chromium to a greater or lesser extent and all of the additives tried were more or less successful in the incorporation of particles in the deposits. Particles included in deposits on vertical surfaces tended to average somewhat smaller in size and to be slightly less numerous than in deposits on horizontal surfaces under similar conditions. In general, it was found that for best wear resistance, a minimum amount of additive should be used, particle concentration of over 60 g/l was of little or no benefit, plating conditions about 55° and 50 asd usually resulted in fewer inclusions with the most effective range 40°/20 asd to 45°/30 asd. Wear was not directly proportional to hardness or the amount of inclusion. Good wear resistance required a continuous chromium matrix with well distributed hard particles. Diamond particles resulted in the best wearing properties with aluminum oxide generally the lowest in wear resistance, although the latter was more easily incorporated than most particles tried.

The main objective of some experiments was the development of a practical bath and procedure for the incorporation of hard particles in chromium on a more or less production basis. A bath-life test was run to determine the effect of additives and particles on the longevity of the chromium plating bath. Ammonium nitrate was effective as an additive in the chromium bath-life test and only after several thousand ampere-hours per liter of bath did deterioration of the bath begin as evidenced by the decreased wear-resistance of the deposits. As a practical experiment, a gun tube was plated with chromium incorporating hard particles. In addition to chromium, deposits of cadmium and zinc were made which included hard particles in cyanide baths. Test deposits were made on vertical cathodes of copper or steel and were heat-treated after deposition to check the effects of heating on wear, adhesion, and structure of the deposit. Particles were included in the cadmium and zinc deposits without additives although addition of thallium salts to the zinc bath increased the amount of particles included.

EXPERIMENTAL-EQUIPMENT

The specimens were prepared in a one liter vessel immersed in a water bath for temperature control. The bath was heated by a radiant heater and cooled during high current density runs by chilled water running through a coil immersed in the water bath. The anodes were formed from lead sheet to conform roughly to three types of cathodes used. The first type was made from stainless steel and "L" shaped to present both vertical and horizontal areas for deposition. For maximum uniformity of deposition, a one-quarter inch diameter copper rod was made concentric vertically with a cylindrical lead anode. Neither of these cathode configurations was suitable for abrasion testing, so for most of the tests (unless otherwise stated) a circular, flat cathode of 25-30 mil thick copper sheet was used. It roughly fitted the diameter of the plating vessel and was initially suspended horizontally near the bottom of the vessel. The perforated lead anode was positioned about one inch from the cathode and parallel to it whether in the horizontal or vertical position.

The electrolyte was agitated by a magnetic stirrer with the stirring magnet beneath the cathode and by an air tube immersed to about the level of the anode. Continuous stirring was necessary to maintain uniform temperature of the electrolyte and keep the particles in suspension. A cover prevented excessive loss by spray and evaporation and supported the air line, as well as a thermometer and the anode (Fig. 1). Current was supplied by full wave, rectifiers with bridge type circuits for minimum ripple.

The circular cathode fitted the Tabor Abraser unit used to test the plated chromium coating for wear resistance. Abrasive wheels used for most of the tests were of the rubber bonded abrasive type (CS-17). Hard vitrified abrasive wheels (H-10) were used for some comparative testing but mostly to prepare a smooth, uniform surface on the specimens to obtain comparative results with the rubber bonded wheels (Fig. 2). Cross-sections were prepared, using standard specimen plastic mounting and polishing equipment, for hardness measurements and photomicrographs. Hardness of cross-sections of the specimens was measured on a Wilson microhardness tester with readings in Knoop Hardness Numbers. Visual microscope examination and photographs were made on a Bausch and Lomb research metallograph. Some early specimens were examined on a Steroscan scanning electron microscope with attached Princeton Gamatic nondispersive spectrometer.

PROCEDURE

The specimen cathodes were prepared by applying an insulating stop-off lacquer to areas not to be plated, the side away from the anode and edges. The surface was then scrubbed with fine pumice and/or dipped in hydrochloric acid solution to remove oxide films from copper.

The electrolyte was made up according to the composition desired and heated before introducing the specimens. Particles which were very fine and showed a tendency to agglomerate were dispersed in water by a high-speed blender before addition to the electrolyte. The bath was then vigorously agitated with the magnetic stirrer, while heating, to keep the particles in suspension. When the desired temperature was reached, the cathode and anode attached as a unit to a cover were lowered into the bath, the rectifier leads attached and plating commenced. Additions to the electrolyte, such as thallium nitrate were then made after dissolution in water. There was evidence that some of the additives were made ineffective by contact with the strongly oxidizing chromic acid solution, so in addition to being added after deposition started, some, especially thallium, were added in increments during the usual four-hour run.

After plating, specimens were measured by micrometer for deposit thickness and checked visually. Those to be tested for wear-resistance were smoothed mechanically with abrasive paper if the surface was other than very smooth. It was found to be very important to have the surfaces of all specimens to be wear-tested as uniformly smooth as possible to obtain consistent and comparable results. To this end the specimens were "worn-in" on the wear tester for several thousand revolutions, using the hard vitreous bonded wheel, if necessary, and the rubber bonded wheel before the actual wear test was made (Fig. 2). Since the wear-test was the one most important test for evaluating the deposits, it was done very carefully. Thickness of the deposits was such that the wear-test could be repeated if desirable. The test consisted of 10,000 revolutions of the specimen under the two abrasive wheels of the abrader with a weight of 450 grams on the surface of the specimen at the point of impingement of each wheel. A magnification of the surface of an abraded chromium deposit containing inclusions is shown in Figure 3. Before each test a fresh surface was obtained on the abrasive wheels by running them on abrasive paper. Most of the later specimens were subjected to an additional test and then checked against the first run. If a lower value was obtained the specimen was deemed to not have been sufficiently prepared initially and the lower reading was used. Wear was determined by weight loss of the specimen to a tenth of a milligram. On completion of the wear-test the 3 3/4 inch diameter specimen was cut in half. The deposit was dissolved in HCl from one-half of the specimen. Inclusions in the resulting chromium chloride solution were filtered out, dried and weighed to determine the percent of particles included. A small section from the edge of the specimen was mounted in plastic for microscopic examination and hardness measurements. Photographs were made of the cross-sections of specimens which appeared to be of interest, such as those containing voids, particles, unusual grain structure, etc.

TESTS AND RESULTS

Initial Experiments

The initial part of the work consisted of trying a wide range of plating conditions and chromium plating bath concentrations in an effort to include particles in the deposit. It had first been determined that particles could be deposited in a nickel matrix from the nickel bath without difficulty. Chromium bath composition and plating conditions were varied as follows:

OrO_3 - 125 to 550 g/1

$CrO_3:H_2SO_4$ - 100:0.5 to 100:1

Current density - 20 to 100 asd (with and w/o superposed AC on some tests)

Temperature - 48 to 80°C

With and w/o mechanical and/or air agitation of bath

Cathode-vertical and horizontal

In addition to the above variations, such procedures as stopping deposition periodically to allow particles to settle on the cathode and periodically reversing the current for a short period were tried.

None of these bath concentrations or plating conditions resulted in significant deposition of particles on vertical or horizontal surfaces. What were thought at first to be inclusions in the chromium deposit on examination of the cross-sections of the deposits were later decided to be voids in the chromium or possibly inclusion of other material, such as oxides of chromium, lead peroxide or lead chromate from the anode (Fig. 4), because of negative analytical results for the intended inclusions.

The next approach was to try additions of monovalent cations which in the highly acidic copper sulfate bath had been found to enhance the codeposition of fine bath-insoluble inorganic particles[3]. Therefore, thallium compounds were tried in the chromium bath, although thallium chromate precipitates quantitatively from chromium solutions. Thallium chloride was first used, as it was available. It formed thallium chromate in the bath and apparent voids were formed in the deposits similar to those in figure 4. Thallium sulfate was avoided to prevent distortion of the critical sulfate ratio in the chromium bath. Thallium nitrate salts were then obtained and used as the addition to furnish the thallium ion. The salt was added as a water solution but most of it was precipitated as thallium chromate and only about 0.2 g/l was soluble in the bath. This is likely a factor in the small amount of material included during codeposition from the chromium bath without formation of voids or excessively rough deposits.

Early tests using 5-10 g/l thallium were disappointing because of the deleterious effects on the properties of the chromium deposits, mainly the reduction of hardness, and the small amount, usually less than 0.5%, of particles included in the deposits. Later, more effective current density-temperature conditions and thallium concentrations were found and the performance of deposits from baths containing thallium improved.

Bornhauser Bath

It had been thought that the acidity of the chromium bath inhibited the effect of the thallium. Work by Tomaszewski, et al[3], indicated that higher pH and Na^+ ions favored codeposition of particles. This inforamtion suggested a chromium bath with a higher pH commonly known as the Bornhauser bath. The composition of the bath was as follows:

CrO_3 - 400 g/1
H_2SO_4 - 0.8
NaOH - 58

Since the main difference between the standard bath and the Bornhauser bath was the sodium hydroxide content, this was added in increments to a standard bath to determine the affect of increasing pH. Runs were made at 10, 20, 40 and 60 g/1 NaOH plus 20 g/1 silicon carbide powder at 60°/40 asd with no thallium. No appreciable effect was noted until the NaOH concentration was 60 g/1, as shown below:

NaOH	Inclusions in Cr	Hardness	Wear Loss
10 g/1	0.13 wt. % SiC	882	9.1 mg
20	0	1005	9.4
40	0.03	1021	8.3
60	10.0	243	7029.2
0	0 (no SiC in bath)	935	5.6

At first it was thought that the action of the thallium in codepositing was enhanced by the Bornhauser bath, but it was later found that the increase in included material was related to the spongy nature of the deposit formed when non-soluble powders were introduced to the bath (Fig. 5). Actually, the higher the concentration of thallium ion the lower the amount of particle codeposition. This is opposite to the effect found in the standard hard chromium bath (Fig. 6). The performance of coatings from the Bornhauser bath, despite the high particle content, was disappointing. The deposits were soft and the higher the percentage of inclusions the more porous and granular the deposits became, until coherence was lost. At 19% silicon carbide the deposit was too granular to permit a wear test. At 10% silicon carbide the wear was an exhorbitant 7.03 grams and the hardness only 243 KHN_{200}. With no particles in the bath the wear was 0.0246 g and the hardness 460 KHN_{200}. Although later tests with the CrO_3 content of the bath under better control gave somewhat harder deposits, the deposits from the Bornhauser bath were usually too soft to have good wear resistance despite included hard particles. With a low (5 g/l) concentration of particles in the bath the addition of thallium to the Bornhauser bath seemed to improve the hardness and thus the wear resistance of the deposits having comparable amounts of inclusions, as shown by the following summary of test results:

$TlNO_3$	Inclusions	Hardness	Wear Loss
0 g/l	0.79 wt. %	367 KHN_{200}	36.3 mg
5	1.15	580	25.4
10	0.69	655	6.9
0	1.63	343	34.2

Codeposition of Metal Powders

The Bornhauser bath was used successfully for the codeposition of several metal powders in chromium. At 60°/40 asd using 5 g/l $TlNO_3$, 8% tungsten powder was included in a deposit on a horizontal cathode, but the hardness of the composite was only 157 KHN_{200} and the wear loss a high 0.29 gram. On vertical cathodes the amount of inclusions were less, but deposit properties were better. For example, at 60°/40 asd and with 10 g/l tungsten powder in the bath the deposit hardness was 761 KHN_{200} with 1.7% included materials. The same conditions plus 5 g/l $TlNO_3$ gave a deposit hardness of 299 KHN_{200} and 0.2% metal powder included for tungsten and 735 KHN_{200} and 0.05% inclusions for nickel. These results with $TlNO_3$ using a vertical cathode in the Bornhauser bath are more in line with results under similar conditions with SiC particles and a horizontal cathode where $TlNO_3$ adversely affects codeposition than are the results mentioned above for metal powders on a horizontal cathod plus $TlNO_3$.

The standard 400 g/l CrO_3, 4 g/l H_2SO_4 bath plus 5 g/l $TlNO_3$ was also used to deposit metal powders with the results shown below:

Metal Pwder.	Cath.	$TlNO_3$	Included	Hardness	Wear Loss
10 g/l Ni	Hor.	5 g/l	4.6 wt. %	373 KHN_{200}	46.4 mg
10	Hor.	0	0.14	479	15.0
10	Vert.	0	0.06	536	--
10	Vert.	5	0.04	250	--
5 g/l Ti	Hor.	5	1.4	788	52.0
10 g/l W	Hor.	5	0.3	511	11.3

It is seen that some metal powder is deposited with chromium on both vertical and horizontal surfaces; that thallium enhanced the inclusion of nickel on a horizontal surface, but was ineffective on a vertical surface.

Vertical Cathodes

In addition to the tests using a vertical cathode, described above, a series of tests were made to decrease the effects of uneven current density on the codeposition of particles in several baths under varying conditions and determine the effect of bath temperature on codeposition. The cathode was a 1/4 inch diameter copper rod and the anode a concentric cylinder of lead sheet. The bath was agitated during plating by air and magnetic stirrer.

Despite the careful arrangement of the electrodes in the bath, there was some difference in the deposits between the bottom, center and top. Cross-sections of the three locations showed more inclusions and/or voids at the bottom and center than at the top of some of the deposits with variations in structure when thallium was used. Results of the tests of effects of various temperatures at 100 asd in the 400 g/l CrO_3 standard bath are given below:

Temp.	$TlNO_3$	Hardness (KHN_{200})				Particles	Inclusions in Cr
		Av.	Top	Center	Bottom		
45	0	531	423	536	634	0	--
55	0	361	322	456	305	0	--
55	5 g/l	654	761	772	429	100 g/l TiO_2	1.2 wt.%
*55	0	262	292.	328	266	0	--
65	0	622	685	659	641	0	--
65	10	966	925	971	1003	100	Pos. for Ti

*Small (10w) superposed AC current during deposition.

Data from various runs on vertical cathodes usually made in connection with runs on horizontal cathodes using electrodes bent 90° in the 400 g/l standard and Bornhauser* baths are shown below:

Temp/CD	$TlNO_3$	Agitation	Particles	Hardness	Inclusion in Cr
60°/40	0	Air	10 g/l Ni pwdr.	536	0.06 wt.%
60°/40	5 g/l	Air	10 g/l Ni pwdr.	250	0.04
60°/40	5	Air + stirrer	5 g/l dia. pwdr.	605	1.7
60°/80	5 $H_4SiW_{12}O_{40}$	Air + stirrer	5 g/l Ni-dia. pwdr.	556	0.05
*60°/40	0	Air	10 g/l Ni pwdr.	329	0.3
*60°/40	5	Air + stirrer	10 g/l W pwdr.	299	0.2
*60°/40	(residual)	Air + stirrer	10 g/l W pwdr.	761	1.7
*60°/40	5	Air	10 g/l Ni pwdr.	250	0.04

Runs 2 and 3, as well as 5 and 7, indicate the critical effect of stirring of the bath on a vertical deposit. The adverse effects of thallium in the Bornhauser bath holds for the vertical cathode, as well as for the horizontal cathode which is demonstrated by the last four runs.

Codeposition of Diamond Powder

Having had some success with the codeposition of several readily available nonconducting powders, a selection of diamond powders was obtained for further experiments. The size of the particles were 1-5 μm, 6-10 μm (Fig. 7) and 10-22 μm. The last was nickel coated and the smallest size (nominally 15 m) that was obtainable from General Electric Company through the Van Itallie Company. The uncoated diamond particles were tried first, then five grams of the 6-10 μm size were nickel coated in an electroless nickel bath before using in the chromium bath. From our experience with the metal powders it seemed that nickel coating non-conducting diamond particles would increase the percentage codeposited. Runs were made without nickel coating the 1-5 μm size particles, with and without nickel coating the particles of the 6-10 μm size and only nickel coated 15 μm particles. Other tests made with baths containing diamond powder included variations of thallium ion concentration and current density-temperature combinations and use of the Bornhauser bath mentioned previously.

The effect of thallium ions on the inclusions of 6-10 μm diamond particles was proportional to the concentration of thallium. Tests included 2 to 10 g/l $TlNO_3$. Results are shown in figure 8. Varying current density and holding bath temperature at 60°C and with 5 g/l $TlNO_3$ and 5 g/l diamond powder, gave the results shown in figure 9 for the amount of inclusions obtained in both the Bornhauser and standard baths. A heavily etched, nodular chromium deposit surface with imbedded diamond particles is shown in figure 10.

Several tests were run with and without nickel coating on the diamond particles. The amount of inclusions was definitely increased by nickel coating using a number of plating conditions. Twelve runs with uncoated particles averaged 0.45 wt.% diamond inclusions in the chromium deposits while ten runs with Ni coated particles averaged 1.19 wt.% with some overlapping of data. Segregating the results obtained from three sizes of diamond particles and the nickel coated particles used in several tests gave the values shown in figure 11, which are an average of several runs of each type. The fact that the nickel coated 11-22 µm size shows more than twice the amount of included particles of the 6-10 µm size may be due in part to the quality of the nickel coating rather than purely an effect of the size.

A comparison of the deposits from the standard 400 g/l CrO$_3$ bath and the Bornhauser bath is shown below: (More data on deposits with diamond powder are given in the section on thallium ion concentration.)

Bath	Cond.	Dia. Pwdr. (5-10 g/l)	TlNO$_3$	Included wt.%	Hardness KHN$_{200}$	Wear Loss
Std.	60°/40	6-10 µm	5 g/l	0.17	875	69.3 mg
Std.	60°/40	6-10 µm	5	1.56	592	12.2
Bornh.	60°/40 (mag. stirrer only)*	6-10 µm	5	0.26	598	78.1
Bornh.	60°/40	6-10 µm	5	1.15	580	25.4
Std.	60°/40	6-10 µm + Ni	5	0.12	639	16.9
Std.	60°/40	6-10 µm + Ni	10	3.35	595	14.3
Bornh.	60°/40	6-10 µm + Ni	10	0.69	655	6.9
Bornh.	60°/40	6-10 µm + Ni	residual	0.79	367	36.3
Bornh.	60°/60	6-10 µm + Ni	5	0.64	-	10.4
Bornh.	60°/80	6-10 µm + Ni	5	0.55	652	18.0
Std.	60°/60	6-10 µm + Ni	5	0.08	407	18.2

*All other runs with air plus stirrer.

This series of tests does not show much difference between the standard and the Bornhauser baths in the amount of included particles obtained. However, the effect of higher thallium ion concentration is more pronounced in the standard bath. The Bornhauser bath appears less sensitive to current density variations which could be important when plating a service item. The deposit from the Bornhauser bath with 10 g/l TlNO shows surprisingly good wear resistance and may result from a hardening effect that can occur with a relatively low concentration of particles in the bath. This effect was noted in a deposit from the standard bath plated at high current (100 asd). A striking difference in the appearance of cross-sections is noted in figure 12 between deposits with (b) and without (a) 5 g/l $TlNO_3$ in the bath under otherwise similar conditions. The diamond inclusions in B averaged about 1.6 wt.% of the chromium.

A test was made of the effect of variation of the current density on inclusions from a standard 200 g/l CrO_3 bath at 55°C plus 1 g/l $TlNO_3$ and 18 g/l of 15 μm, nickel-coated diamond powder. Figure 13 shows the resulting wear loss (the values at 50 asd were the best obtained thus far) and hardness of the deposits. The weight percent of inclusions in the chromium deposit ranged from 0.39 for 40 asd to 1.32 for 60 asd.

Soluble Additives

The data obtained up to this point in the work indicated that hardness of the chromium matrix in which the particles are deposited was an important factor in the wear properties. Since the use of thallium and the inclusion of particles almost invariably reduced the hardness of a chromium deposit, including those with excellent wear resistance, soluble additions to the electrolyte were tried which had been reported to have hardened and increased the wear resistance of chromium . The most effective chemicals described were potassium permanganate ($KMNO_4$) and silicotungstic acid ($H_4SiW_{12}O_{40}$). The $KMNO_4$ was added to a 400 g/l CrO_3 bath containing no particles and the $H_4SiW_{12}O_{40}$ was added to a 200 CrO_3 bath containing 10 g/l SiC. Initial tests showed no marked improvement in hardness of the deposit with or without the thallium ion present as shown below in lines 1 and 2, 6 and 7, 4-5 and 14:

$H_4SiW_{12}O_{40}$ g/l	$TlNO_3$ g/l	Temp./CD	Inclusion wt.%	Hardness KHN_{200}	Wear Loss mg
0	5	65°/40	1.75	297	10.3
5	5	65°/40	2.41	336	9.9
5	5	55°/50	1.57	471	9.8
1	0	55°/50	0	1054	9.3
1	0	55°/50	0	1067	6.3
0	1	55°/50	0.30	785	15.3
1	1	55°/50	0.25	599	11.5
1	2	55°/50	0.41	560	18.3
1	3	55°/50	0.48	641	33.2
1	4	55°/50	0.51	533	24.2
1	5	55°/50	0.88	609	16.8
2	2	55°/50	0.08	545	7.6
3	3	55°/50	0.41	688	13.7
9	0	55°/50	0	1053	7.9
$KHMO_4$					
40	0	30°/20	0	817	12.5

Figure 14 is a graphical representation of the effect on the amount of included particles of increasing the thallium ion concentration in the 200 g/l CrO_3 electrolyte plus 1 g/l $H_4SiW_{12}O_{40}$.

Perhaps the most valuable result of the soluble bath addition tests was the discovery while making a comparative run without soluble addition that 1 g/l $TlNO_3$ was effective in codepositing particles and did so without the usual formation of voids (Fig. 15). Succeeding runs were therefore made with 1 g/l $TlNO_3$ and the best wearing deposits obtained thus far in this work were obtained. Data from these runs are given in the next section.

Effect of Particle Concentration

This test was run with SiC particles because of the limited supply of diamond powder available. The SiC concentration was varied between 10 g/l and 75 g/l. Figure 16 shows the effects of particle concentration on amount of included materials. Other data from the test, including temperature/current density variations, are shown below:

SiC g/l	$TlNO_3$ g/l	Temp./CD	Inclusions wt.%	Hardness KHN_{200}	Wear Loss mg
10	1	55°/50	0.30	785	15.3
20	1	55°/50	1.41	614	3.4
30	1	55°/50	0.98	608	3.6
50	1	55°/50	0.68	871	7.5
75	1	55°/50	1.07	639	4.6
75	2	65°/40	0	653	32.6
75	2	65°/60	0.55	644	7.8
75	2	65°/80	0.08	889	15.2

The effect of even a small amount of inclusions on wear is demonstrated by the runs at 65/40 and 65/60. The former yielded no inclusions and showed up poorly in the wear test. The latter deposit contained only about one-half of one percent SiC but wear is 75% less for about the same deposit hardness.

Controlling Thallium Ion Concentration

The cross-sections of a number of deposits showed the inclusions grouped in a band or layer parallel to the basis metal. Sometimes the band was quite narrow or it could have the width of one-half of the deposit thickness as in figure 17. Apparently the thallium ion was used up or rendered ineffective a short time after its introduction to the plating bath. Higher concentrations of thallium initially usually caused excessive distortion of the deposit as in figure 19, but with most of the particles still in a band of limited width. Introduction of the $TlNO_3$ increments might result in more uniform distribution of the hard particles and thus improve wear performance. Tests were run varying the amount of $TlNO_3$ added per unit time and the total amount used for a test. Figure 20 shows the particle distribution achieved by adding the $TlNO_3$ in three increments with one-half the total amount (1 g/l) added as the first increment. Figure 21 shows the effect of varying the number of equal additions during the 4-hour plating time from 2-16. Some tests were also run using unequal additions as initial deposits indicated a minimum concentration below which no codeposition occurred. The data obtained from several of the tests at 55°/50 and with 75 g/l SiC in the 200 g/l CrO bath are shown below:

Increments	Total $TlNO_3$ (g/l)	Inclusions wt.%	Hardness KHN_{200}	Wear Loss mg
2	1	1.07	639	4.6
4	1	0.63	607	13.3
8	1	0.32	663	14.0
16	1	0.06	1071	11.1
8	0.5	0.19	995	8.5
8	0.25	0.07	1040	5.6
4	1(dilute)*	0.02	1067	7.4
3 (3/4 first addn.)	1	0.29^{+}	595	8.7
3 (1/2 first addn.)	1	0.18^{+}	443	4.0
3	1	0.43^{+}	507	2.6^{o}

[*] $TlNO_3$ dissolved in 480 ml H_2O before adding to bath, 48 ml H_2O used in other tests.

[+] 18 g/l Ni-coated, 15 μm diamond powder used in these tests.

[o] This deposit gave less than one-half the wear loss of the best deposit without inclusions.

These data indicate that there is a relatively narrow range between minimum and maximum concentration of the thallium ion for effective codeposition of particles in the chromium deposit at a given set of plating conditions. The table shows that a minimum concentration of $TlNO_3$ must be maintained in the bath to effect codeposition of particles. With the addition of amounts of 1/16 g/l or less the concentration of $TlNO_3$ in the bath was apparently below the effective minimum.

Plating Conditions and Thallium Concentration

A number of deposits using 30 g/l boron carbide in the bath with varying amounts of thallium nitrate and at various temperatures and current densities were tried in an effort to expand the range of conditions for effective incorporation of particles in chromium and to, perhaps, find conditions resulting in a deposit with wear-resistance superior to previous results. Previous work indicated that a chromium plating bath containing 200 g/l chromium trioxide and 2 g/l sulfuric acid was advantageous in several ways so these concentrations of the basic constituents were used for all the tests during this period. At least 1/2 g/l thallium was dissolved in water and placed in the bath at the beginning of the run and the remainder, if any, was added in equal increments during the course of the run.

Figure 26 summarizes our results for the amount of included B_4C in the chromium as a function of the thallium concentration, the temperature, and the current density. That the data suggests only vague trends or correlations is evident. This may be, in part, because the particle inclusion is not very sensitive to the three operating variables. It may also be because the experiments were not highly reproducible. This is suggested by the duplicate values plotted in Figure 26, which show a sizable spread. This lack of reproducibility was given considerable attention and we have been unable to identify the cause. The current density, temperature, and bath geometry were closely controlled. We believe our analytical method is satisfactory. Agitation is nominally the same, maintaining particles in suspension continuously. The trivalent content of the baths is gradually changing, though maintained within limits, and this may be significant. Also, the possible build-up of decomposition products of the additives during operation and aging of the bath may be a factor, as well as variations in depletion rate under varying conditions of operations.

The data show that inclusions are found in the chromium if thallium is present. It suggests that 0.1 to 1% of inclusions will be obtained with 1 to 5 g/l thallium at 30°/20 asd to 65°/75 asd.

The effect of thallium concentration alone on the wear-loss and hardness of chromium deposits with no particles added to the bath is shown in Figure 27. The spread of temperature and current density combinations giving a wear-loss of about 6 mg or less per 10,000 abrader cycles is shown in Figure 28. The concentrations of thallium nitrate in the bath for deposits having a wear-loss of less than 6 mg are plotted in Figure 29. It may be noted that a slightly lower average weight-loss was obtained with 3 g/l thallium. There were other deposits plated using the same bath composition and conditions which did not have similar low weight-loss values.

These exploratory tests of temperature, current density and thallium concentration variations did not reveal a set of conditions more beneficial than those previously tested. It has been observed that at the higher temperature-current density condition a given amount of thallium results in the incorporation of fewer particles (Fig. 26) and has a less deleterious effect on the properties of the chromium deposit. Conversely, about twice as much thallium may be used at 55°/50 asd as at 40°/20 asd without causing excessive discontinuities or granular chromium deposits that are useless.

Various Types of Particles

Several types and sizes of particles were used for incorporation in chromium deposits in an effort to obtain maximum wear resistance as follows:

Diamond	- 5, 10 and 15 μm (Previously reported)
Silicon carbide	- 25 μm (Previously reported) and 15 μm
Aluminum oxide	- 5, 9.5 μm and fumed (very fine - "Alon")
Zirconium silicate	- 40 μm
Boron carbide	- 15 μm
Silica	- fumed (very fine - "Cab-O-Sil")

The following data show the overall average wear resistance for those deposits containing 0.1 wt.% or more of particles, including all plating conditions and amounts of additive used:

Particle	Size μm	Nominal Particle Hardness (KHN)	Number Deposits in Average	Least Wear-Loss mg	Average Wear-Loss mg
Al_2O_3	5	2000	9	11.6	16.7
Al_2O_3	9.5	2000	11	6.2	11.4
Alon	--	--	11	6.1	12.8
B_4C	15	3000 - 5000	45	2.0	7.9
C (diamond)	10	7000	14	2.6	6.9
C (diamond)	15	7000	7	2.6	5.7
Cab-O-Sil	--	--	6	14.8	18.2
SiC	15	2500	9	3.8	15.6
SiC	25	2500	18	3.4	8.6
$ZrSiO_4$	40	--	7	5.5	15.7

Although the best wear for a single deposit is for one containing B_4C, the more significant best average wear is for deposits containing diamond particles. Of course, absolute optimum conditions may not have been selected for any or all types of particles because of practical limits to the number of tests that could be run, but we believe that the general relative merits of the particles have been obtained. A summary of the individual tests as regards additive concentration, particle concentration and plating conditions and their effect on the amount of particles included is shown in Figure 30. It suggests that the concentration of particles in the bath caused changes in the amounts of $ZrSiO_4$ and Al_2O_3 - 5 μm included in deposits.

The average wear resistance of deposits with incorporated B_4C (shown in the tabulation above), though not as good as that for diamond, was better than the wear resistance for any of the other particles tried. Therefore, B_4C should have favorable consideration for use as a practical wear-resistant particle for inclusion in chromium deposits.

Various Additives

Several additives were tried in addition to thallium that would hopefully promote increased incorporation of particles in the deposits while having a lesser deleterious effect on the properties of the chromium. The following monovalent cations were tried: cesium, lithium, ammonium and sodium. Again, there is no certainty that the absolute optimum conditions have been used, but the general relative performance of each is shown below:

Additive	Number of Runs in Average	Most Inclusions (wt.%)	Average Inclusions (wt.%)	Least Wear-Loss (mg)	Average Wear-Loss (mg)
$TlNO_3$	21	1.54	0.43	3.2	7.6
$CeNO_3$	22	0.88	0.43	3.5	9.6
$CeNO_3$ + $TlNO_3$	4	0.65	0.39	3.5	5.0
$LiNO_3$	7	0.67	0.41	7.8	12.4
$NaNO_3$	7	1.85	0.88	3.8	17.4*
NH_4NO_3	1	--	.68	--	11.3

*Five deposits in average.

Several deposits were made using ammonium nitrate as an additive, but in only one was an amount used which produced a continuous chromium plate. More tests with this additive should be made. In comparing the average performance of the various additives there are several factors that should be kept in mind. The results for thallium and most of the results for cesium were from deposits on horizontal surfaces. At this point a series of tests were made on vertical surfaces. It was found that almost equal amounts of inclusions could be obtained in deposits on vertical surfaces (as is shown in the next section) so the remainder of the additives were used in conjunction with vertical cathodes. The results for thallium are from deposits with included boron carbide while those for cesium included some runs with aluminum oxide and silicon carbide as well. Therefore, considering the slightly better wear performance of boron carbide, the results of thallium and cesium are very close. For practical use, thallium would probably be the choice of the two as the price of cesium salts is about four or five times that for thallium. A few runs on a vertical cathode (Fig. 31) indicated cesium is slightly more effective than thallium in incorporating silicon carbide in a chromium deposit. Figure 32 shows the slightly greater disruption of normal chromium structure by thallium than by cesium. This poorer deposit contains discontinuities (large irregular dark areas with no "trail" of raised chromium), rougher surfaces and fissures near surface.

The three other additives: lithium nitrate, sodium nitrate and ammonium nitrate, all seemed to have a more deleterious effect on the properties of the chromium for equivalent amounts added than did thallium or cesium (Fig. 33). However, used in smaller quantities, they were effective in including particles in the deposits. Figure 31 summarizes some of the results obtained in relation to the amount of additive used. These additives are much less expensive than thallium or cesium and should not be ruled out for practical use. One of them ($NaNO_3$), when used for including particles, has shown that it can result in better wear than standard bright chromium. Figure 34 compares chromium structure at two levels of sodium nitrate concentration with about the same amount of included material in each deposit. The deposit made with the greater amount of sodium additive is believed to contain some discontinuities in the chromium in addition to inclusions.

Vertical Cathodes

At one point in our investigation, a number of tests were made to determine whether electrodispersion of particles in chromium could be a practical process for general application to articles other than flat pieces that would involve vertical surfaces as well as horizontal areas. Several tests were made on vertical surfaces using thallium in the chromium bath. Overall results are shown below:

	Particle	No. Runs	Maximum Inclusions (wt.%)	Average Inclusions (wt.%)	Least Wear-Loss (mg)	Average Wear-Loss (mg)
Horizontal	B_4C	21	1.54	0.43	3.2	7.6
Vertical	SiC	18	1.62	0.39	4.5	12.4

The better wear performance of horizontal deposits could be at least partially the result of the harder boron carbide particles, although the average of included material in vertical deposits is slightly below that in deposits plated horizontally. Because the results were close and to obtain more data and experience, several of the additive tests were run on vertical cathodes, as indicated above, and all resulted in the effective inclusion of particles (Fig. 35).

Steel as Basis Metal

Several test deposits were made on carbon steel substrates. The steel was plated with and without a preplate etch in the plating solution. Adhesion to the steel was good in both cases, as indicated by 180° bend tests, and no difference in other properties could be detected between these deposits and deposits on the usual copper substrate.

Lubricating Particles

Several tests were made with molybdenum disulfide or fine graphite in the bath alone and in conjunction with hard particles. Deposits from baths containing molybdenum disulfide were very poor and after two or three runs the bath became incapable of producing continuous chromium deposits. As much as 0.12 wt.% of the graphite was included in deposits by using 1 g/l lithium nitrate. Wear-loss averaged 11.4 mg, substantially more than that for bright chromium with no particles.

Various Hard Particles

Up to this point in our investigation, chromium deposits with incorporated diamond particles resulted in the best wear-resistance. The next best wear characteristics were given by incorporated tetra-boron carbide particles. An effort was made to find particles that would impart greater wear-resistance to chromium deposits than B_4C. One of the large abrasive suppliers especially prepared without charge six super-hard particles and a seventh type of hard particle was purchased from another company. The particles were as follows: AlB_{12}, B_4C, B_6C, CrB_2, $5Si_3W_4$, TiB_2, and TiC. The average size of the particles was about 25 µm. Scanning electron micrographs of two of the types of particles (Fig.36) show a rather wide range of sizes which is not considered detrimental for our purpose.

The particle resulting in the best wear of a chromium deposit by a small margin was B_6C. The special B_4C and the AlB_{12} were very close in imparting wear-resistance. Commercial silicon carbide particles of about 15 μm in size were used for comparison. The 200 g/l CrO_3 bath and a vertical cathode were used for all tests. Three or four runs were made using each type of particle at one or two temperature-current densities and with two types of chemical additives. A summary giving the averages of the results for tests of each type of particle is given below:

Particle		Deposit		
Type	Hardness	Hardness	Wear Loss	Inclusions
AlB_{12}	2300 KHN	675 KHN_{200}	7.7 mg	0.18 wt
B_4C	2800	669	7.5	0.27
B_6C	3000	695	6.3	0.30
βSi_3N_4	3000	677	12.9	0.33
CrB_2	3500	604	11.2	0.61
TiB_2	2700	662	7.8	0.59
TiC	2500	640	12.2	0.83
SiC	2500	749	10.2	0.85
Glass powder	----	616	11.3	0.20

The detailed data from the tests indicated that specific combinations of plating conditions and additives resulted in increased inclusion rates of some particles. For example, TiB_2 was included in substantially greater amounts using $LiNO_3$ at 45°/30 asd than at 55/50. Using $TlNO_3$ and $LiNO_3$, larger amounts of TiC were included at 45/30 than at 55/50. These instances conform with the general observation throughout the program that fewer particles are normally included at higher current density and temperature conditions but this is not true for all combinations of particles and additives. Therefore, it cannot be taken for granted that an additive or a set of plating conditions will result in the best particle inclusion rate for a given particle because it is best for several others.

None of these special hard particles showed enough improvement in wear-resistance when included in chromium to warrant their use in place of some of the best of the more readily available particles already tested although the B_6C shows some superiority over all the others tested except diamond.

During the tests of the CrB_2 particles, some of the thallium and cesium additions to the chromium baths were made in the crystal form. The usual procedure was to add these components as a water solution in four equal increments during the run. Additions as crystals did not form the usual yellow precipitate and the effectiveness of the additives seemed to extend throughout the run of 4 or 5 hours without partial periodic addition to the bath as had been previously practiced. In a water solution of CrO_3 the crystals were observed to dissolve very slowly.

Bath Life Test

The initial phase of this test consisted of eight runs. A new bath was used for each of the first three runs; then five consecutive runs were made in the same bath. All eight tests were made with 30 g/l B_4C and 3 g/l $TlNO_3$ in the baths. The wear-resistance was good for the three runs in the new bath, about one-half the weight loss for hard, bright chromium without inclusion, and the results are quite close. The tests in the "used" bath indicate a slight decrease in wear-resistance for each successive run as an increasing amount of current is put through the solution as shown in Fig. 37. Bath component concentration levels were maintained and no substantial decrease in the amount of included material in in the deposits occurred throughout the test. Since the trivalent chromium content of the bath remained within acceptable levels, it is probable that the slight decrease in wear-resistance of successive deposits was due to build-up in the bath of Tl or Tl compounds. Deposits and amounts of included material did not appear to be adversely affected.

The second phase of the bath-life test consisted of 58 tests for a total of 5100 ampere-hours per liter of chromium plating solution. Components of the solution were renewed as necessary to maintain the nominal bath composition of 200 g/l CrO_3, $2H_2SO_4$ and 30 g/l B_4C. Ammonium nitrate at 1 g/l was used as the monovalent cation additive for most of these tests. Near the end of the experiment several tests were made without addition of NH_4NO_3 and hardness of the chromium deposit returned to about 100 KHN_{200} and inclusions in the chromium dropped below 0.1 wt.% indicating approximately normal deposits that would be expected from a standard chromium bath. However, after about 3200 amp-hours per liter had been passed through the bath, the spread of wear-resistance values obtained increased substantially (as shown in Fig. 38) and the average wear-loss had about doubled at the end of the test or at 5100 ampere-hours. There were visible encrustations on areas of the bath container where the bath was subject to evaporation. This was assumed to be the result of the build-up of NH_4NO_3 or its decomposition products. It was definitely not CrO_3. At the end of this series of tests, a total of nearly 40 grams of NH_4NO_3 had been added to the bath.

The above indicates that there is probably a limit to the life of a chromium bath when using NH_4NO_3 as an additive beyond which deposit properties would not be acceptable. For all practical purposes even 3200 ampere-hours per liter of bath represents a very long bath life in the practical chromium plating bath. In addition it is entirely possible that the products of the additive could be removed from the bath by a simple procedure such as cooling and decanting as they seem to be much less soluable than CrO_3.

During the bath-life experiment the use of a new wear-test abraser was started. Comparison of the results obtained on the new and old machine showed some difference in wear-resistance values so a factor was used to make results compatible.

Various Additives

A number of runs were made using the additives previously tested to some extent. As indicated in the section above, NH_4NO_3 was used in a considerable number of tests and was found to be effective for incorporating particles in chromium deposits. However, the bath would tolerate only about one-third as much NH_4NO_3 as $TlNO_3$ and still produce continuous, hard deposits. More runs were also made using $LiNO_3$ and $CeNO_3$ and, of course, $TlNO_3$. A general summary of the relative performance of the additives during these tests is shown in Fig.39 and is tabulated below:

Additive	No. of Runs in Av.	Most Inclusions (wt %)	Av. Inclusions (wt %)	Least Wear-Loss (mg)	Av. Wear-Lo (mg)
NH_4NO_3	39	3.89	0.762	3.9	8.2
$LiNO_3$	12	2.29	0.60	6.4	11.3
$CeNO_3$	4	1.65	1.26	8.2	10.0
$TlNO_3$	45	1.41	0.41	3.0	8.6

All of the above deposits were made on vertical surfaces but include several different types of particles and plating conditions of from 45°C/20 asd to 55/50. Several, but not necessarily all, of the conditions were used for each type of additive. Figs. 39 to 41 show the relative amounts of inclusions and wear-loss respectively for lithium nitrate as compared to thallium nitrate for runs under similar conditions. The lithium shows wider fluctuations in both categories than does thallium nitrate.

Corrosion Protective Deposits Containing Hard Particles

Cadmium. A number of cadmium and zinc deposits were made which incorporated B_4C and Al_2O_3 hard particles in an attempt to improve the wear-resistance of a soft, protective coating. No chemical additives were needed to include particles in cadmium and zinc deposits although one-half to one gram per liter of thallium salts in the bath increased the amount of included material in zinc.

The cadmium specimens were plated in a bath of the following nominal composition:

Cadmium oxide, CdO	22.5 g/l
Sodium cyanide, NaCN	100
Sodium hydroxide, NaOH	14
Gulac (organic grain refiner)	0.4

To this bath was added the Al_2O_3 and B_4C in varying amounts from 10 to 30 g/l. The current density used for a particular deposit seemed to have more effect on wear-resistance than the type or amount of hard particle incorporated. All runs were plated at about 24°C. Below is a summary of the cadmium deposits tested:

Current Density (asd)	No. Runs	Type of Particles	Max. Inclusions (wt %)	Av. Inclusions (wt %)	Least Wear-Loss (mg)	Av. Wear-Loss (mg)
1	2	--	--	--	53.8	55.9
1	2	B_4C	0.69	0.67	29.4	39.1
2	4	"	1.06	0.98	19.3	23.9
3	1	"	--	1.11	--	27.8
4	1	"	--	1.48	--	32.0
5	1	"	--	1.08	--	25.2
1	2	Al_2O_3	0.58	0.38	53.8	64.7
2	4	"	0.64	0.58	33.3	43.8
3	3	"	0.88	0.62	34.8	36.3
5	1	"	--	0.60	--	47.1

The improvement in wear-loss for deposits with included particles was better than two to one over deposits without particles for the best series of tests. The B_4C particles were incorporated more readily and resulted in the greatest improvement in wear-resistance. Average inclusions per run for B_4C was 1.06 wt %, for Al_2O_3, 0.55 wt %. Average wear-loss for B_4C was 29.6 mg, for Al_2O_3, 48.0 mg. Figs. 42-44 are graphic presentations of data from tests of Cd deposits. Refinement of bath composition and plating conditions could quite possibly further improve the wear-resistance of cadmium coatings.

Zinc. The zinc bath used had the following composition:

Zinc sulfate, $ZnSO_4$	240 g/l
Ammonium chloride, NH_4Cl	15
Ammonium sulfate, $(NH_4)_2SO_4$	30
Licorice (grain refiner)	1

To this bath up to 30 g/l B_4C and Al_2O_3 particles were added. Also, several tests were run in a zinc bath containing thallium salts as well as hard particles which did increase the amount of inclusions in the deposits. A series of runs was made in the zinc bath with varying amounts of particles in the bath and at several current densities as well as a few runs using thallium. A summary of the tests is shown below:

Current Density (asd)	No. Runs	Type of Particles	Max. Inclusions (wt %)	Av. Inclusions (wt %)	Least Wear-Loss (mg)	Av. Wear-Loss (mg)
2	2	--	--	--	34.9	36.5
3	2	--	--	--	40.6	42.0
2	1	Al_2O_3	--	0.13	--	23.4
3	4	"	1.05	0.50	30.3	42.9
5	1	"	--	0.13	--	22.5
2	3	B_4C	1.96	0.99	20.5	25.9
3	5	"	0.43	0.31	19.5	23.2
5	2	"	0.59	0.43	26.0	26.7
2	4	B_4C+Tl	1.82	0.78	21.0	27.7
3	6	"	1.79	0.98	17.4	23.3
5	2	"	0.58	0.53	23.0	25.2

Since the current density seemed to have more effect on the wear-loss than the amount of particles in the bath, all runs at a particular c.d. were averaged together from baths containing ten to thirty g/l of particles. The improvement in wear-resistance for deposits containing hard particles was not as great as for cadmium but there was some improvement at 2 and 5 asd with Al_2O_3 and with B_4C in the bath. (See Figures 46-48 for graphic representations of the data.)

Thallium increased the amount of included material at 3 asd but was not effective in these tests at 2 and 5 asd. Wear-resistance was very close with or without thallium, about two-thirds that of deposits without inclusions. Average inclusions per run with Al_2O_3 was 0.32 wt %, with B_4C, 0.70 wt %. Average wear-loss for Al_2O_3 was 36.6 mg, for B_4C, 25.0 mg. Data from deposits formed with thallium in the zinc bath are shown graphically in Figures 49-50.

Gun Tube

A 0.30 caliber machine gun tube furnished by the Rock Island Weapons Laboratory was plated on the inside with chromium incorporating hard particles by adding thallium and B_4C powder to a standard 200 g/1 CrO_3 bath. First, several steel tubes of approximately the same inside diameter as the gun tube were plated experimentally to determine the correct equipment or fittings and plating conditions necessary to obtain a more or less uniform coating on the tube bore. To obtain approximately the same deposit thickness distributions as the original chromium plate in the tube bore, 0.0033" at the muzzle and 0.0025" at the breach, it was necessary to form a one-eighth-inch diameter anode from pure silver wire and then copper and lead plate it for protection from attack. Using this anode and a temperature-current density ratio of 45/30, it was found that a reasonably uniform deposit incorporating B_4C particles could be applied to the simulated gun tubes. The gun tube bore, plated in a vertical position at these conditions, had a deposit thickness at the muzzle of 0.0031" and at the breech, 0.0027". The simulated gun tubes were sectioned and revealed inclusions of hard particles in the rather rough deposit even at the top of the tube. Fig. 51 shows cross-sections at the top and the bottom of one of these test specimens in which the distribution of the chromium was rather poor but otherwise similar to the deposit in the gun tube. It was later learned that the chromium deposit with incorporated particles in the gun tube was broken from the bore surface rather quickly under firing test conditions without much of a determination of its "wearability."

Heat-Treated Deposits

Several particle-containing chromium deposits plated on copper were heated in air to determine the effect, if any, on adhesion to the substrate and wear qualities. After heating,mild bending of the specimens cracked the chromium but no flaking, indicating loss of adhesion, occurred. Wear-resistance was somewhat diminished on those deposits heated above 250°C as is shown in the data below:

Initial Wear-Loss	Heat-Treatment	Resultant Wear-Loss (mg)
12.8	400°C - 1 hr	17.3
13.8	" " "	17.3
10.6	600°C " "	15.5
13.6	250°C 2 "	12.9

The normal heat-treatment of chromium plated parts to relieve possible hydrogen embrittlement of the substrate is in the 200-300°C range so chromium deposits with included particles should not be adversely affected. Cross-sections of the heated deposits are shown in Fig. 52.

Reactions of $TlNO_3$

Several tests were conducted in an effort to better understand the action of the thallium ion in promoting particulate codeposition in chromium. A solubility test revealed that about 0.2 g/l of $TlNO_3$ dissolved in a 400 g/l chromic acid plating bath at room temperature. Slightly more went into solution at plating temperature. The remainder formed thallium chromate (Tl_2CrO_4). Tl_2CrO_4 introduced to a warm, fresh plating bath of similar concentration dissolved in the amount of 6% by weight or a little over 0.1 g/l. This does not explain the severe effect on the chromium deposit when thallium is used in the higher concentrations of 5 to 10 g/l.

Further isolation of the reaction was attempted by depositing chromium from a bath containing thallium and with the cathode and anode separated by a porous ceramic partition. After 60 ampere-hours of electrolysis, the thallium chromate precipitate was recovered from the anolyte except for about 0.2 g/l which was presumed dissolved. This agreed with the solubility test described above. An accurate measurement was not made in the catholyte because of other material formed during electrolysis.

Thallium chromate introduced into a plating bath in a porous envelop resulted in having no effect on the deposit discernable as a change in structure, appearance, properties or the codeposition of particles. Results of these tests were not very informative and further checking is planned.

DISCUSSION

With the simple addition of particulate matter (SiC, TiO_2, diamond, Al_2O_3, etc., powder) to a conventional chromium plating bath, there is very little codeposition of the particles. By adding $TlNO_3$ to the bath as others have done with other plating systems, we were able to codeposit the particles in significant quantities. Unfortunately, most of our deposits had a poor wear resistance compared to ordinary hard chromium. These deposits were made over a wide range of plating conditions. If we consider those deposits with a wear rate of less than 9 mg (standard chromium 55°/50 asd, 200 g/l) (Tables on pp. 15 and 16) we note that 2 g/l or less of $TlNO_3$ were used in every case. Whenever 5 or 10 g/l was used in the conventional bath, the effect on wear resistance was negative. Our data is not sufficient to pinpoint the optimum range of thallium nitrate addition, as related to current density and bath temperature.

A graph of wear vs inclusions (figure 18) taken from the first five lines of data in the table on page 15, shows a close relation between wear and particulate inclusions for a given system; that is, if everything else is the same. It appears that when other variables are changed, the wear changes, as with current density (figure 13). Hence, to obtain good wear qualities, more than just the amount of codeposition must be considered. The process by which the particles were incorporated into the deposit is critical.

The nature or properties of the codeposited particles is, of course, a factor also. But how important is this factor? With the present achievement of 2% or less codeposition in the best wearing deposits, only a very small percent of the deposit surface (the wearing surface) consists of exposed particles. The balance of the surface is chromium with its own wear characteristics and it can be expected to wear away between the included particles, at least by the Taber Abraser with the semi-rigid, rubber-bonded abrading surface, but which is more responsive to the amount of included particles than the hard, vitrious-bonded wheel mentioned earlier in this report.

The mode of action of the thallium nitrate is not clear. Presumably the partial solubility of thallium chromate provides ions which were adsorbed on the particulate matter and perhaps the solid chromate has the detrimental effects. In any case, a better understanding of this reaction could facilitate improvement of the process.

In other plating systems, cations other than Tl^+ are effective, though Tl^+ is stated to be the most effective. Perhaps another ion would be more effective than Tl^+ in the chromium bath. Na^+ has been found effective in a copper bath, hence, we included the Bornhauser bath in our experiments. Apparently it works insofar as codeposition is involved, but the basic wear properties of the Bornhauser chromium are poor. It may be possible to formulate a suitable chromium plating bath in which sodium ions will be effective and the deposit will be more wear resistant.

A summary of the effects obtained by the inclusion of particles from a variety of chromium baths and plating conditions is shown in figures 22-31. By plotting the bar graphs with hardness on one side and wear loss opposite, the distance between the inside ends of the bars is a general representation of the effect of the included particles on wear resistance. For example, a deposit with high hardness would have good wear resistance and the hardness bar would extend far to the left. The wear loss bar would be shorter than for a softer deposit but the distance between the ends of the bars would not be as great as it would for a short bar for a soft deposit and a short wear-loss bar because of included particles. Although the distance between the ends of the wear-loss and hardness bars is not in every case entirely due to the effect of the included particles, an overall picture of some of the various tests can be seen. Generally, those deposits showing poor wear but having appreciable amounts of inclusions contained the inclusions in voids or agglomerates, or were chipped or cracked.

The experiments , using additives, have shown an inertial and a residual effect. That is, the full effect of the additive is not realized during the first run in a bath with no previous addition. Also, a bath that has been run with an additive will continue to codeposit particles (occasionally in larger amounts) for one or more runs, as though an addition had been made. This residual effect is usually considerably reduced after one run without a new addition, but is sometimes effective enough to include some particles for several runs. The effect can be eliminated by heating the bath to 80°C for an hour or more and by the process used for reducing trivalent chromium ions to hexavalent ions during which the bath is also heated to about 80°C and operated at high cathode current density.

For a given amount of included particles, low temperature and current densities require the least amount of additive and at these conditions the physical properties of the chromium are more seriously affected by a given amount of additives. These lower temperatures and current densities (40°/20 asd to 45°/30 asd) are the conditions most likely to be useful for practical applications of chromium with included particles. Although regular chromium is harder at 55° and 50 asd, when enough additive is used for the effective inclusion of hard particles, there is little difference in hardness between deposits plated with high or low temperature-current density conditions.

The effect on the chromium deposits of all the additives tried was the same except for degree. A given amount of cesium salt appeared to degrade the properties (cause discontinuities, fissures, roughness, low hardness) of the chromium to a slightly lesser degree than did thallium for the same conditions (Fig. 33). Lithium salts seemed to have the most deleterious effects on the chromium properties of all the additives tried (Fig.39), but by using smaller amounts a suitable deposit having included particles could be obtained. The effects of other additives ranged between those of lithium and thallium.

The amount of particles included in the deposit at a given set of conditions also affected the properties of the chromium. Included material in amounts much over 1% of the weight of the chromium had a deleterious effect in addition to that of the additive on the hardness, structure, and probably therefore the wear-resistance. Data obtained from some deposits with over 1% particles show that for seven deposits with an average of 3.1 wt.% inclusions, the average hardness was 281 KHN_{200}. There were no wear-test results because of discontinuous deposits or the deposits wore through before completion of the test. Not all deposits with more than about 1 wt.% of inclusions were soft and discontinuous, but of those that could not be wear-tested most had more than 1 wt.% included material. These poor deposits were usually formed during tests of larger amounts of additive or when the bath had a high concentration of trivalent chromium. Those deposits having wear-resistance more than that for hard, bright chromium (about 6 mg for 10 K abraser cycles) almost always contained between 0.1 and 1.0 wt.% of particles. The average amount of included particles in 22 deposits showing improved wear over standard chromium was 0.39 wt.%. This could be an indication of the approximate amount of particles to aim for in practical applications.

It was noted that particles remaining in the bath over a substantial period of operation were less likely to be incorporated in the deposit than freshly added particles, so a small amount of fresh particles were added to the bath before each run. These small additions compensated for spillage and drag-out losses maintaining the desired concentration.

It was rather disappointing to learn that of the several new types of particles tried, only one showed any improvement in wear-resistance over the previously tested B_4C. The particle giving improved wear when incorporated in chromium was the closely related B_6C and the improvement was only slight. This means that for top wear-resistance diamond powder must be incorporated in the deposits. The expense of using diamond could be reduced by using a smaller amount in the bath without seriously affecting incorporation rates. It is estimated that as little as 10 or even 5 g/l instead of 30 g/l would be effective in the bath. Since the amount usually included in the deposit is 1 wt.% or less, the depletion rate would be minimal. However, in general B_4C and even SiC give improved wear-resistance when included in deposits and would probably be effective for most uses.

Particles are included most effectively at 45°C or below and at current densities of 50 and down to 20 asd with the most effective combination for most selections of additives and particles at 45°C and 30 asd. These conditions result in a deposition rate of about 1 mil per hour and reasonable distribution. If required, higher temperatures and current densities include some particles up to about 65°C and 60 asd.

Some types of particles seem to be more readily incorporated than others. This may be related to their ability to become electrically charged. Shape, size, mass, and adsorption may also have some effect. For example, nickel coated diamond is more readily incorporated than uncoated diamond and SiC and CrB_2 were incorporated more easily and in larger quantities over a range of conditions than some other types that may not be as conductive.

Normally the life of a chromium bath is indefinite, requiring only periodic additions of CrO_3 to replace deposit and drag-out losses. The life test run on the chromium bath containing additives for the including of particles up to 5100 ampere-hours per liter showed that the only problem was a build-up of the additive or by-products of the additive in the bath. When the bath was treated for removal or reduction in concentration of these by-products, it behaved normally again. The only exception was a bath used with lithium nitrate as an additive. It seemed to contribute to the build-up of Cr_2O_3 in the bath and prevent its reduction to CrO_3 again. Deposits from a bath thus affected were dull and rough and uniformity of coverage was poor.

It is considered that in a large plating bath the use of the other additives would not cause any problems as 5100 ampere-hours per liter of bath represents a considerable amount of plating in a particle plating operation.

Further tests of several of the additives used, mainly NH_4NO_3 and $CeNO_3$, confirmed previous results indicating that $CeNO_3$ was most effective for incorporating particles in a chromium deposit with minimal disruption of the structure and characteristics of the chromium. However, it is quite expensive and more common materials such as NH_4NO_3 are inexpensive and adequate for practical operations. Probably the ultimate combination according to present results would be $CeNO_3$ and nickel coated diamond particles added to a 200 g/1 CrO_3; $2H_2SO_4$ bath operated at 45°C and 30 asd for the best wear-resistant deposit.

Particles were incorporated on vertical cathodes in cadmium and zinc deposits from the cyanide baths used without the use of an additive. However, the use of thallium in the zinc bath enhanced the amount of particles included. It was not tried in the cadmium bath. Wear-resistance was more than doubled for cadmium deposits containing hard particles. Wear-resistance for zinc deposits containing hard particles was improved but only by about 30 to 50%. It is possible that variation of mechanical arrangement of the electrodes and bath composition could considerably increase the amount of included material and thus perhaps the wear-resistance

Heating the chromium deposits in air oxidized the exposed copper basis material extensively but only treatments at 400°C and above oxidized the chromium. The reduction in wear-resistance at the higher temperatures was expected as any softening of the chromium matrix reduces wear qualities despite the presence of hard particles which were most likely unaffected by the comparatively low temperatures used.

At the end of the program a few tests were made in a 200 g/l CrO_3 chromium bath using sodium fluosilicate as a catalyst plus an additive and hard particles. Efficiency was very low and only a coarse, greenish colored deposit was obtained which had completely unsatisfactory wear qualities. There was no time to experiment with other fluoride catalysts or plating bath combinations.

This program for incorporating hard particles in chromium deposits has shown that many monovalent cations are effective when added to the bath in amounts of about 3 g/l or less over a range of plating conditions and even on vertical cathodes. Without these additions no particles are included from the standard chromium bath. However, the additives or the included particles or both result in the deposition of softer, dull deposits under plating conditions that would normally yield hard bright deposits. Wear-resistance is improved over bright, hard deposits only because of the presence of hard particles in the chromium matrix. If additives and conditions could be found that deposited bright, hard chromium with included hard particles, it is fairly certain that the improvement in wear-resistance would be many times that achieved in this program.

CONCLUSIONS

The work on this program demonstrated that it was entirely feasible to include hard particles in chromium deposits with a resultant increase in wear-resistance. Other particles such as metal powders and dry lubricating material were incorporated in chromium. Hardness and brightness were diminished when particles were included either because of the presence of the particles or because of the monovalent cation added to the bath or both. Inclusions of more than 5 wt.% of particles seriously degraded all properties of the chromium but even less than 1 wt.% of hard particles in the deposit was effective in reducing wear. Boron carbide particles yielded the best wear, with the exception of diamond, of any particle commercially available with inexpensive silicon carbide a close second. Bath-life was reasonably good and no impediment is seen to scaling up the process for practical application on at least a semi-production basis. Particles were included on horizontal and vertical surfaces as well as on the inside of tubes with suitable internal anodes and with the use of plating conditions within the normal range for chromium deposition.

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LIST OF ILLUSTRATIONS

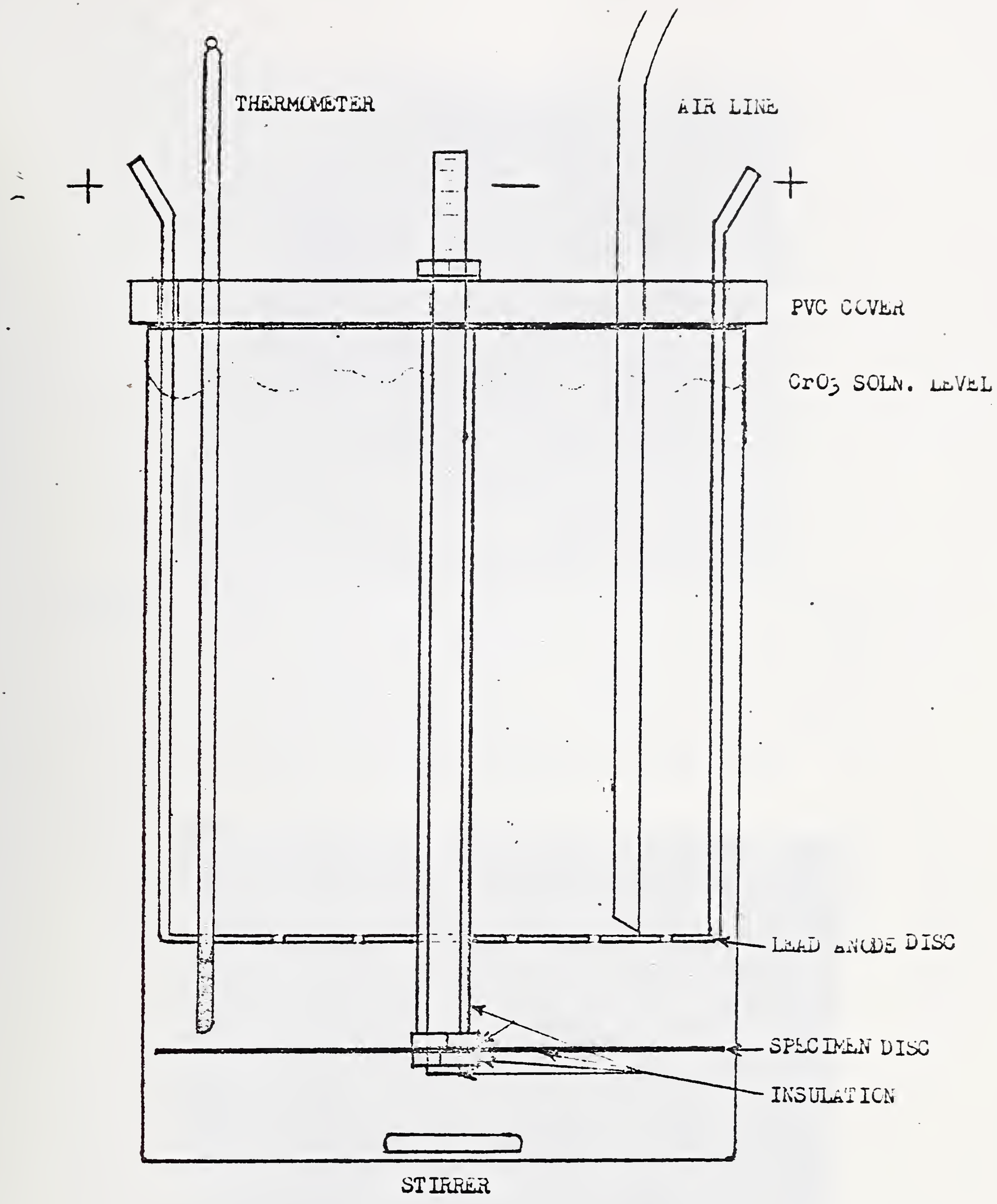


FIGURE 1. Plating arrangement for making deposits on a 3 3/4 inch circular horizontal cathode. Underside of cathode is insulated from plating current as is the cathode supporting rod.

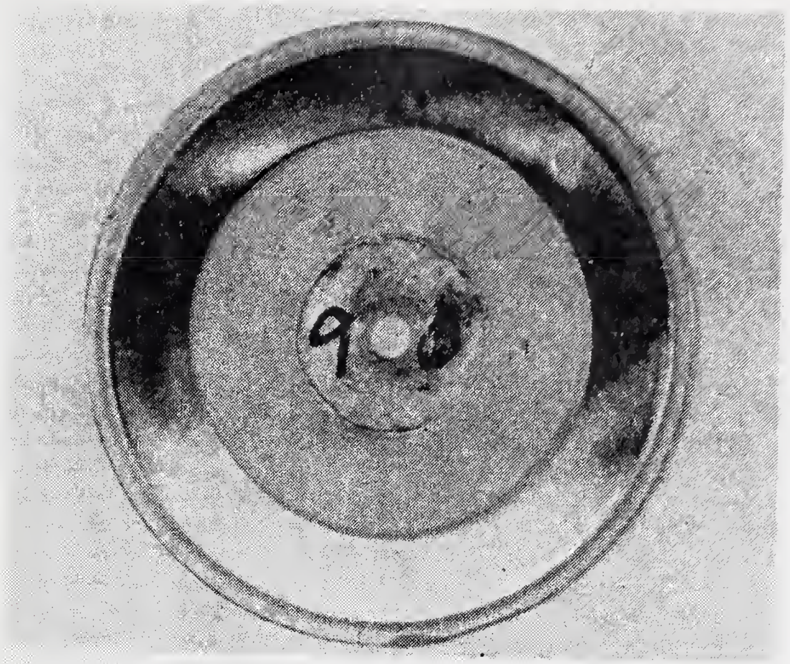


FIGURE 2. Experimental chromium deposit 5 mils thick on 3 3/4 inch horizontal copper cathode disc showing wear track of Tabor Abraser wheels. Center area not plated. Wear resistance of deposit determined by weight loss.

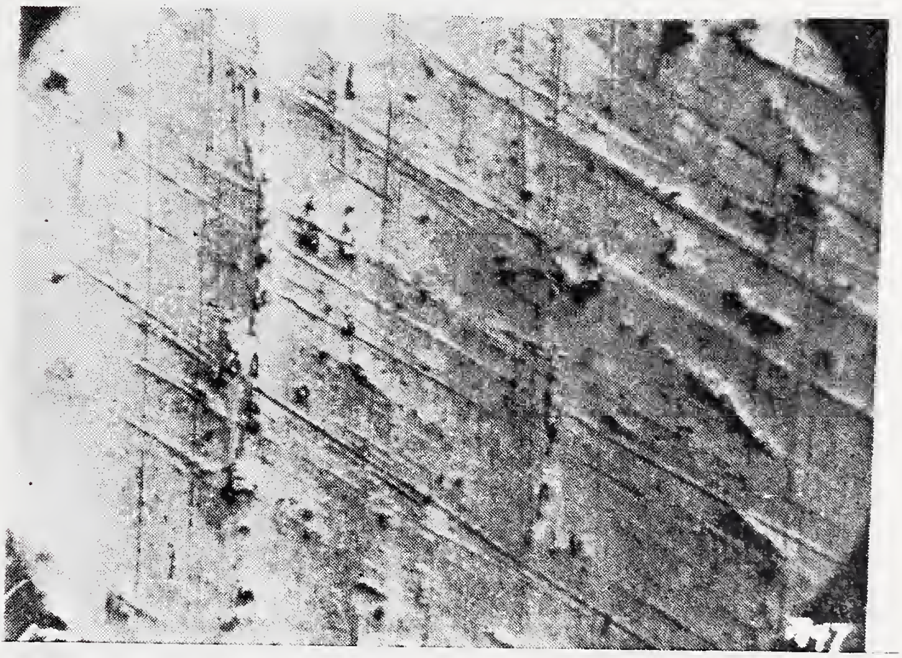


FIGURE 3. Off-center Abraser wheels mark specimen surface at nearly right angles. Deposit contains 0.43 wt.% of codeposited nickel coated diamond particles. Original 350X.

FIGURE 4. Cross-section of deposit that appeared to have inclusion of TiO_2 but gave no positive analytical test for Ti. Dark areas are probably oxides of chromium or small voids in the chromium. Original 550X.

FIGURE 5. Cross-section of deposit plated at 60°/40 asd from the Bornhauser bath plus 20 g/l SiC. Deposit contained 10 wt.% SiC but hardness was only 243 KHN_{200} and wear loss an excessive 7+ grams. Original 350X.

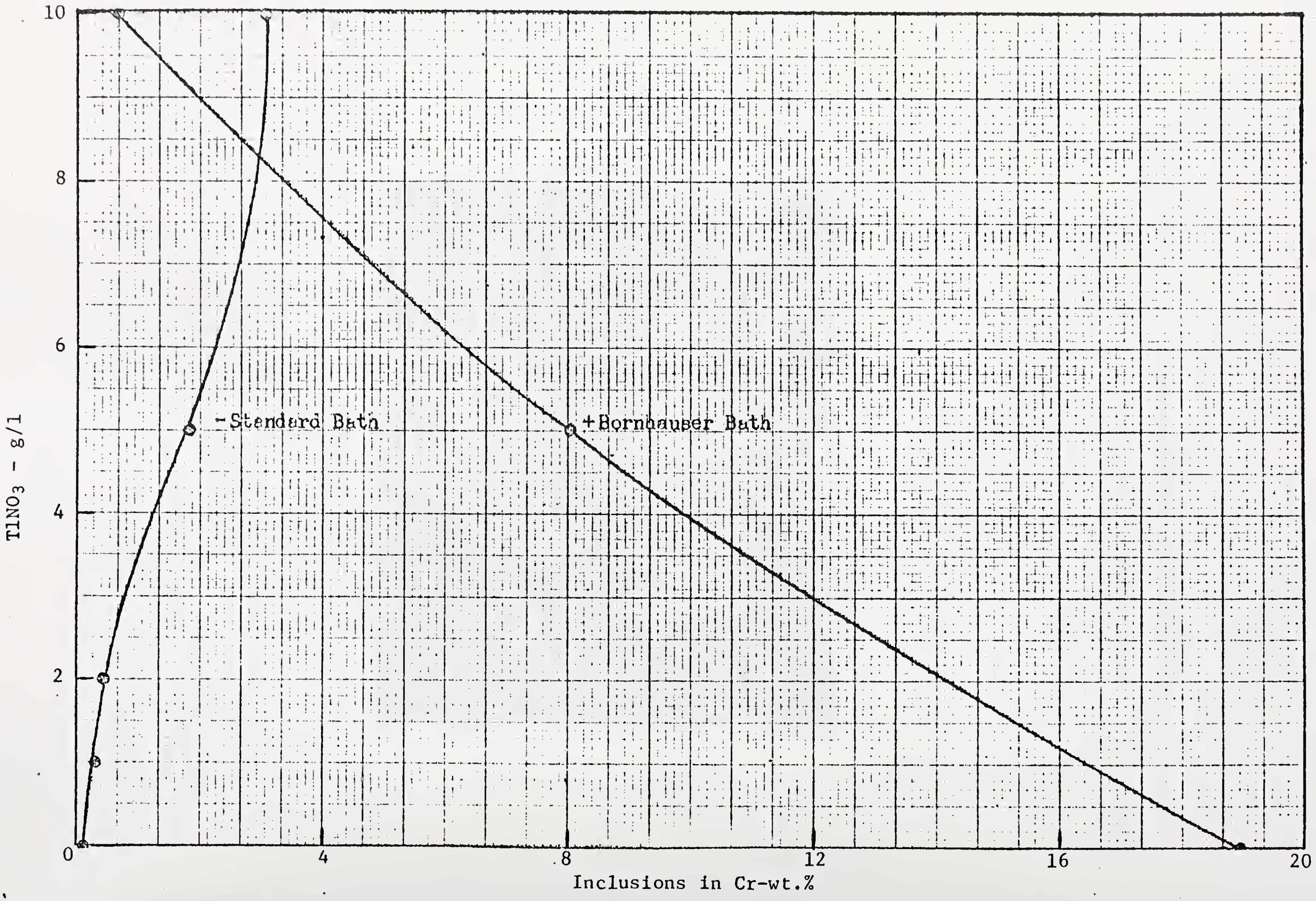


Figure 6. Thallium nitrate concentration versus amount of inclusions in the deposits from the standard 400 g/l CrO_3 and Bornhauser chromium baths. Plated at 60°C and 40 asd with 20 g/l SiC.

FIGURE 7. A scanning electron microscope (SEM) photograph of 6-10 μm uncoated diamond particles. Original 1000X.

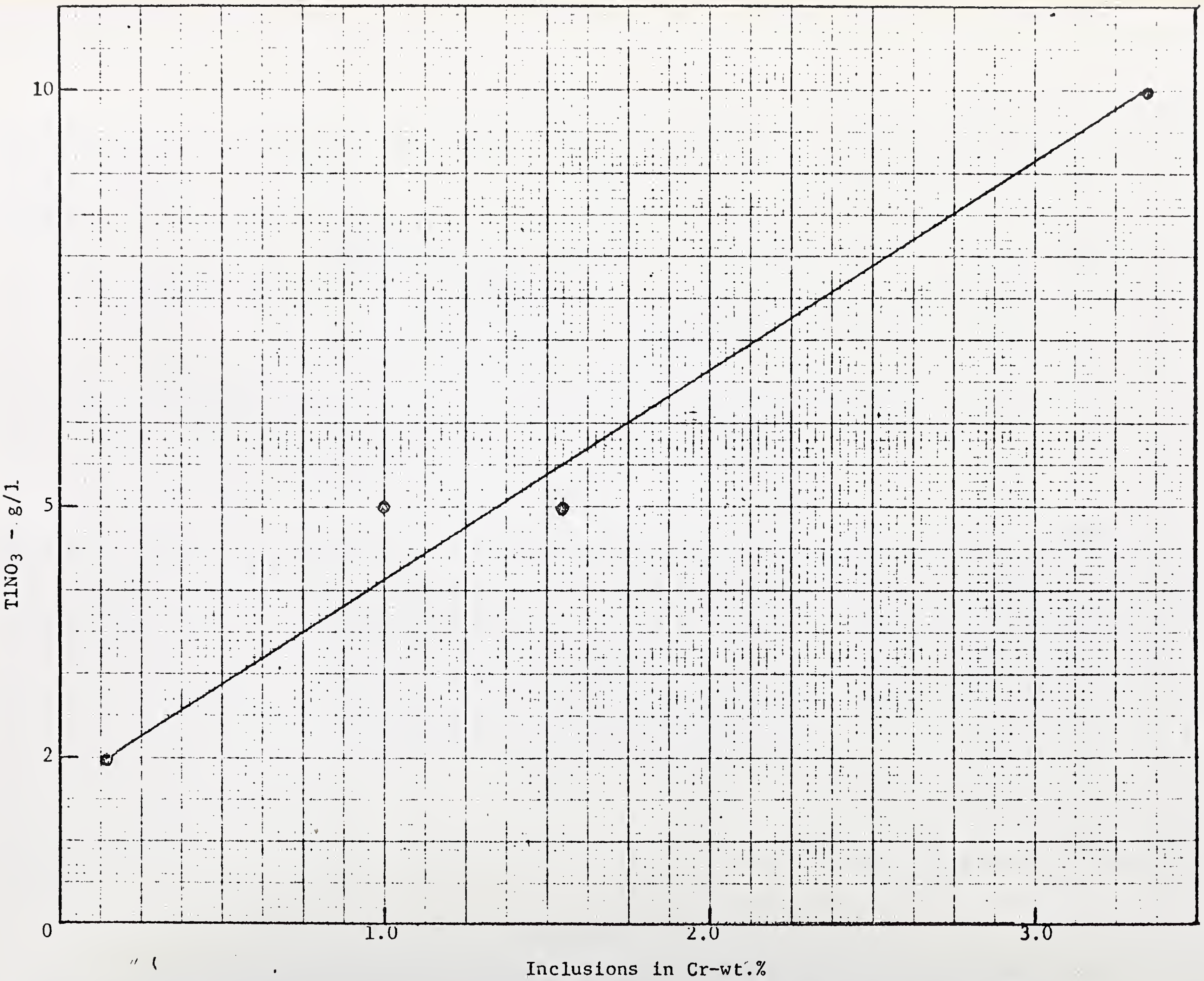


Figure 8. Thallium nitrate concentration versus amount of 6-10 μm diamond particles included in the deposits from the standard, 400 g/1 CrO_3 chromium bath. Plated at 60°C and 40 asd.

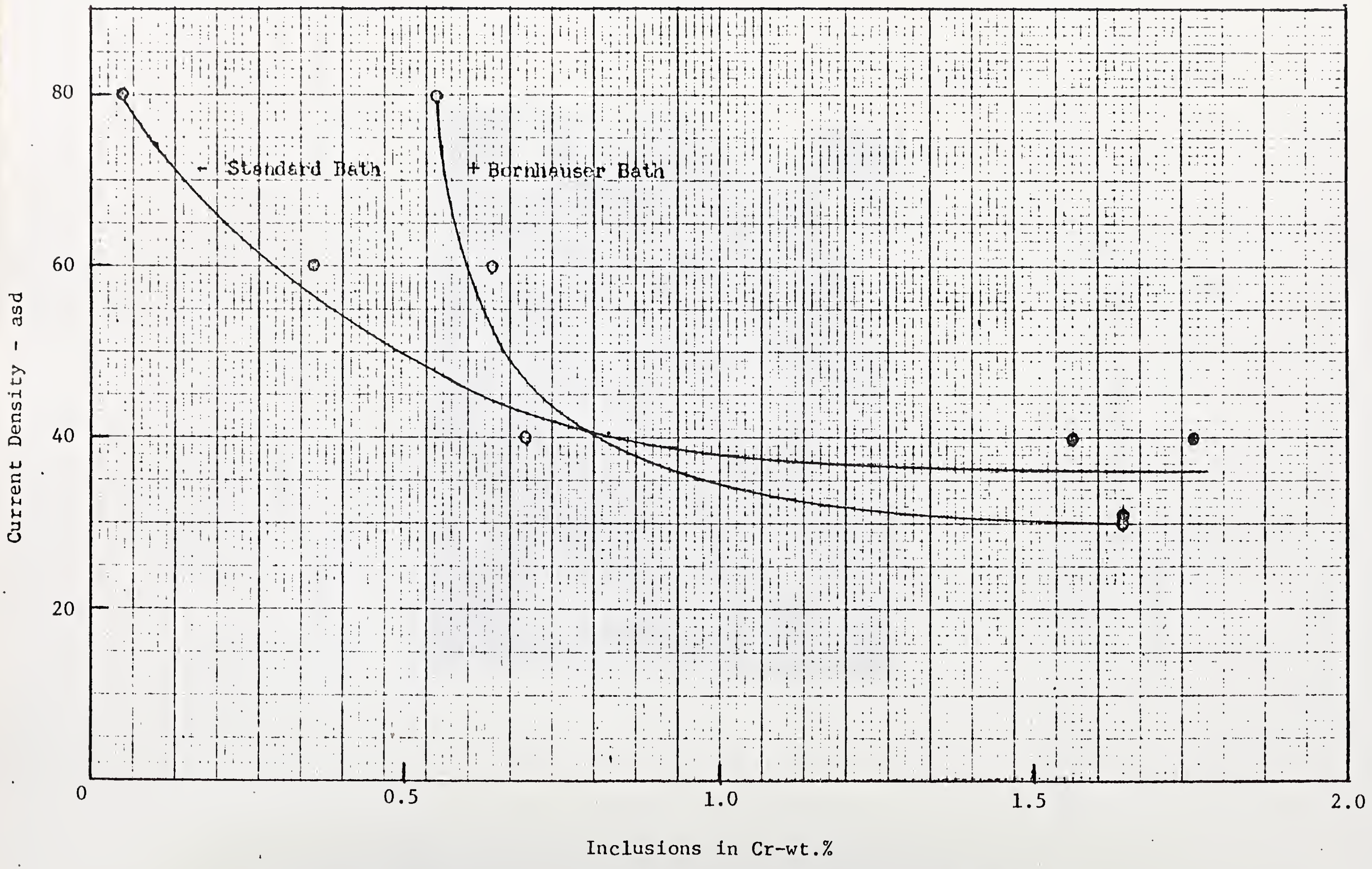


Figure 9. Current density versus the inclusion of diamond particles (6-10 μm) in deposits from the standard, 400 g/l CrO_3 and the Bornhauser chromium baths at 60°C with 5 g/l $TlNO_3$ added.

FIGURE 10. SEM photograph of deeply etched, nodular chromium surface containing imbedded diamond particles. Original 265X.

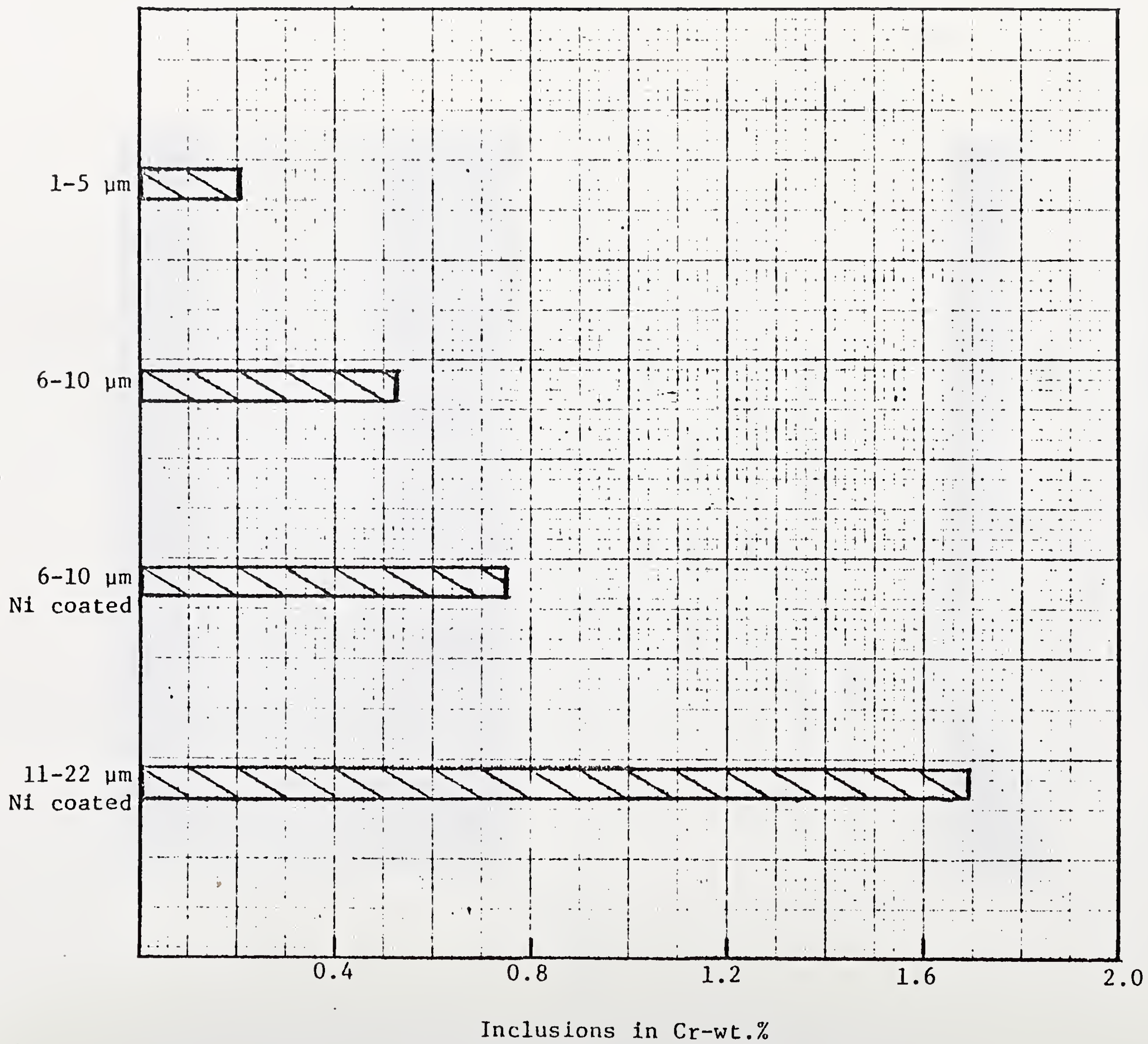


Figure 11. Type of diamond particles used with the average amount of each type included in a deposit on a horizontal cathode plated at 60°C and 40-60 asd in the standard 400 g/l CrO_3 bath plus 5 g/l $TlNO_3$.

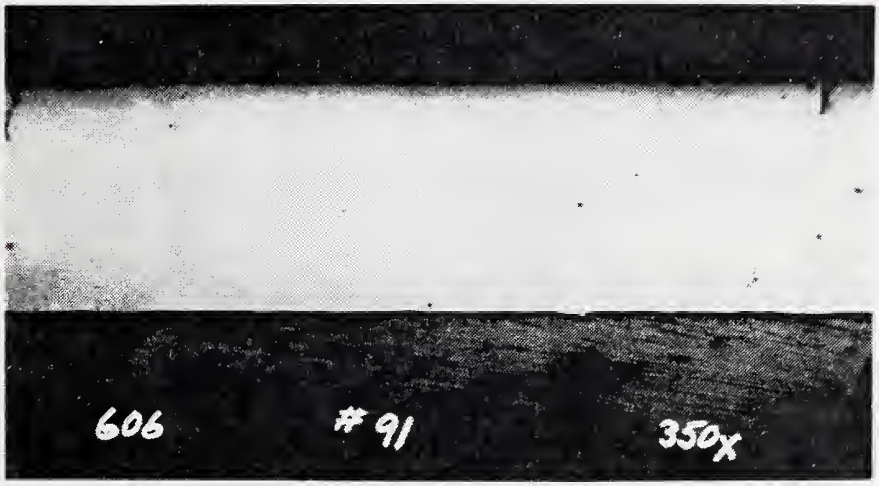
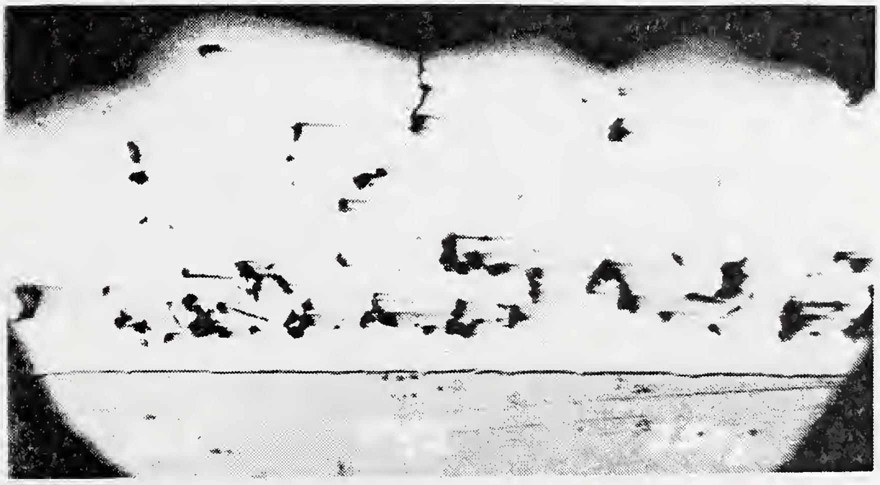


Figure 12 A & B. Cross-sections of similar chromium deposits with (607) and without (606) the addition of 5 g/1 of thallium to the bath. Chromium plated from 200 g/1 CrO_3 standard bath at 60°/40 asd. 607 contains 1.5 wt.% diamond powder. Original 350X.



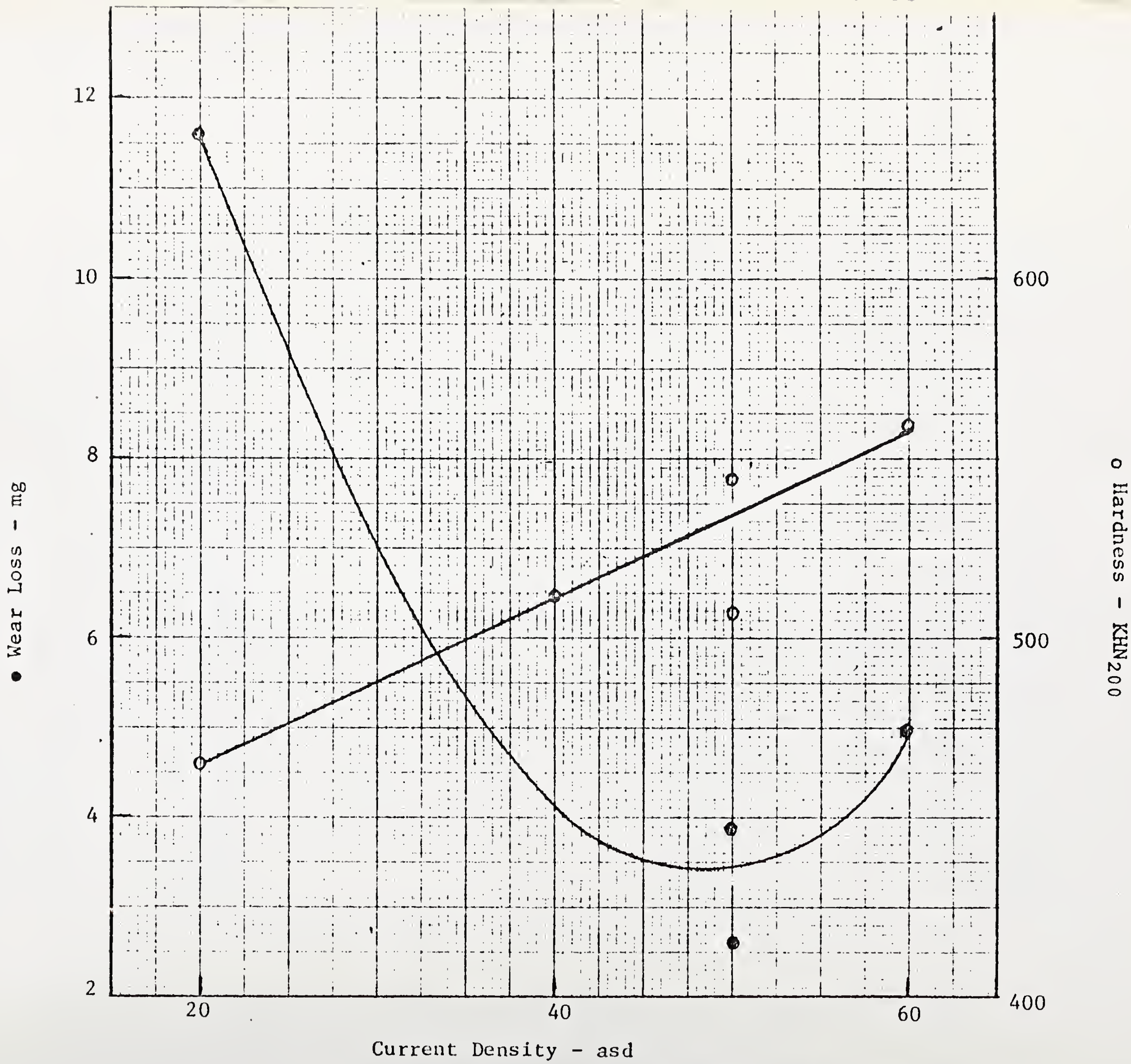


Figure 13. Effect of current density on hardness and wear. Deposits made in standard 200 g/l CrO_3 bath plus 1 g/l $TlNO_3$ and 18 g/l 15 μm nickel coated diamond powder at 55°C.

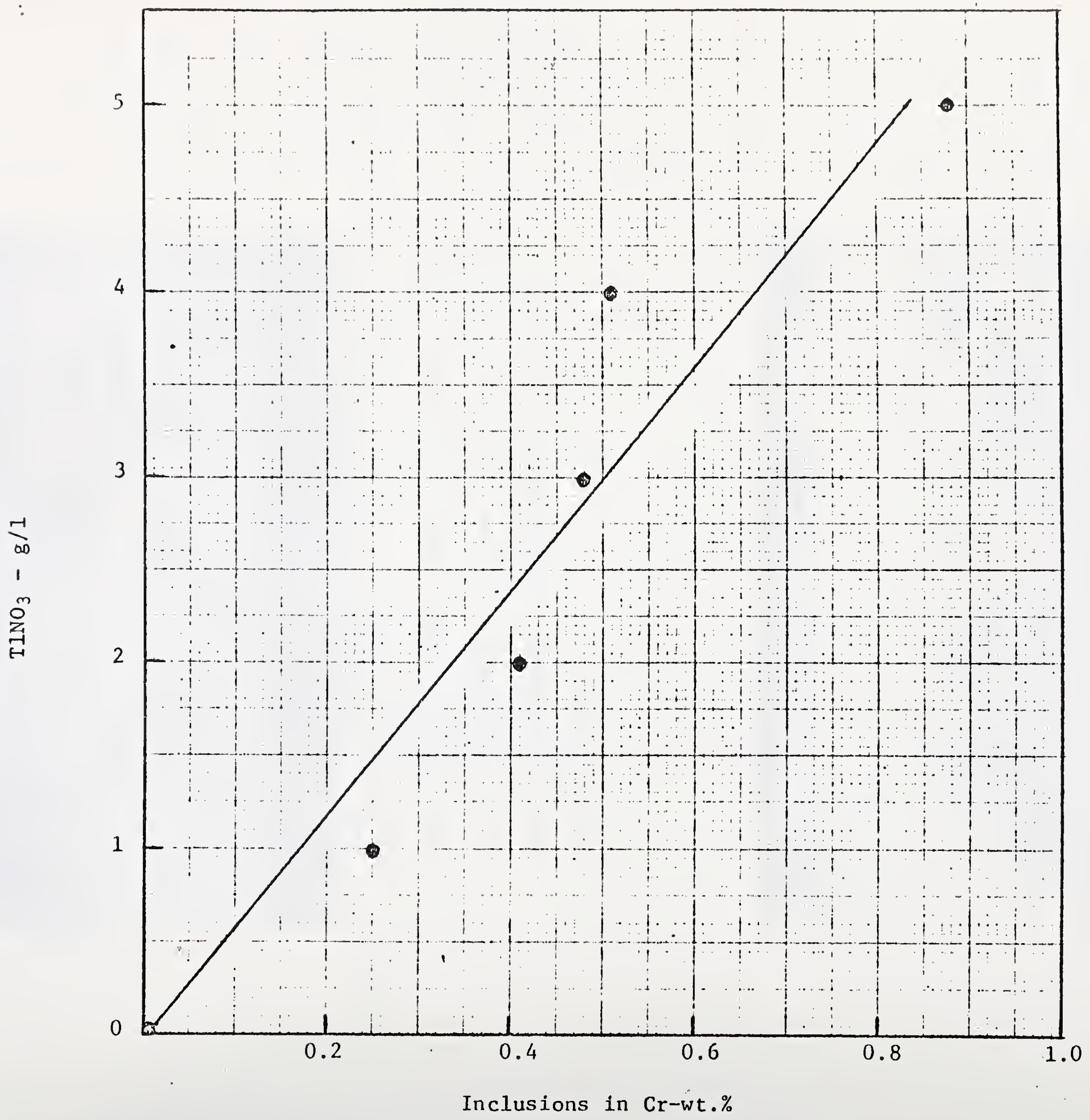


Figure 14. Thallium content of bath versus SiC particle in deposits plated in standard 200 g/l CrO_3 bath plus 1 g/l $H_4SiW_{12}O_{40}$ and 10 g/l SiC particles at 55°C and 50 asd.

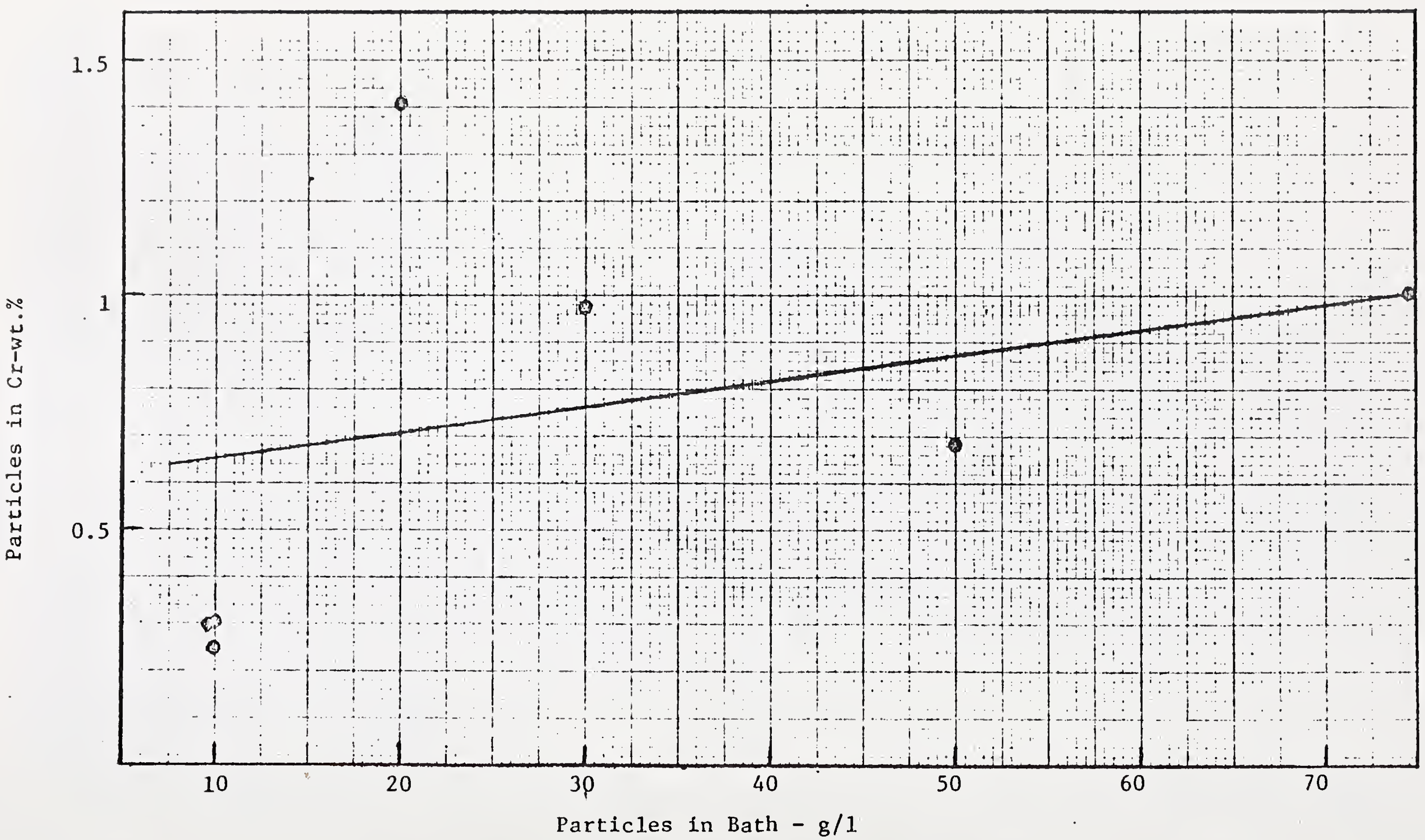


Figure 16. Particle concentration in bath versus SiC particles in deposit plated in standard 200 g/l CrO_3 bath plus SiC and 1 g/l $TlNO_3$ at 55°C and 50 asd.

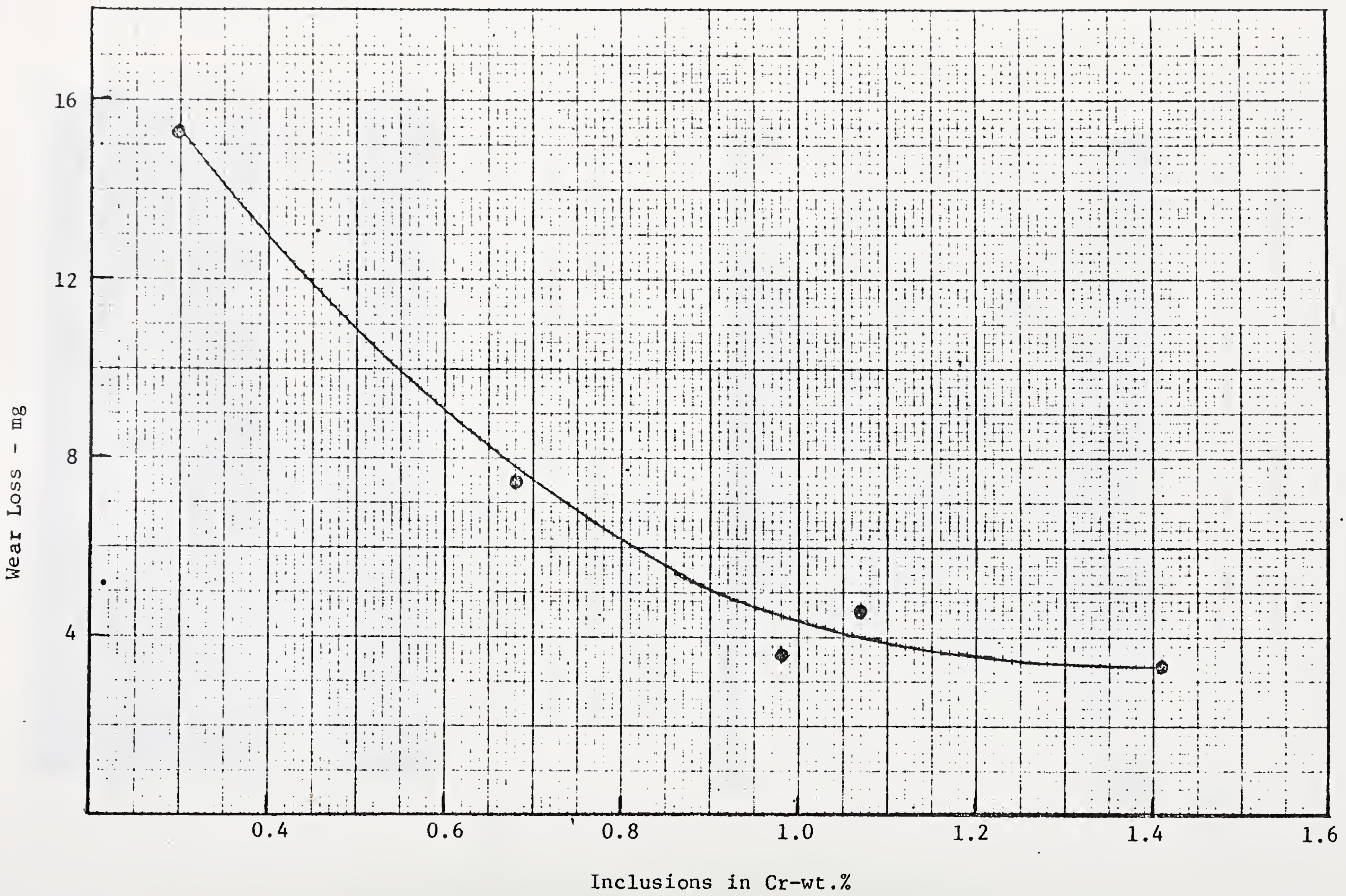


Figure 18. Amount of SiC in deposits versus wear loss of deposits plated at 55°C and 50 asd in the standard 200 g/l chromium bath plus 1 g/l $TlNO_3$ and SiC particles.

FIGURE 19. Cross-section showing distortion of deposit by the addition of 5 g/l $TlNO_3$. Plating had started before addition was made. Deposit contained 1.7 wt.% diamond powder. Original 350X.

FIGURE 20. Cross-section of deposit made with 1 g/l $TlNO_3$ added in increments, one-half first then two additions of one-fourth at equal time intervals. Deposit made in 200 g/l CrO_3 bath plus 18 g/l of 15 μm nickel coated diamond powder at 55°/50 asd and contained 0.18 wt.% diamond. Original 350X.

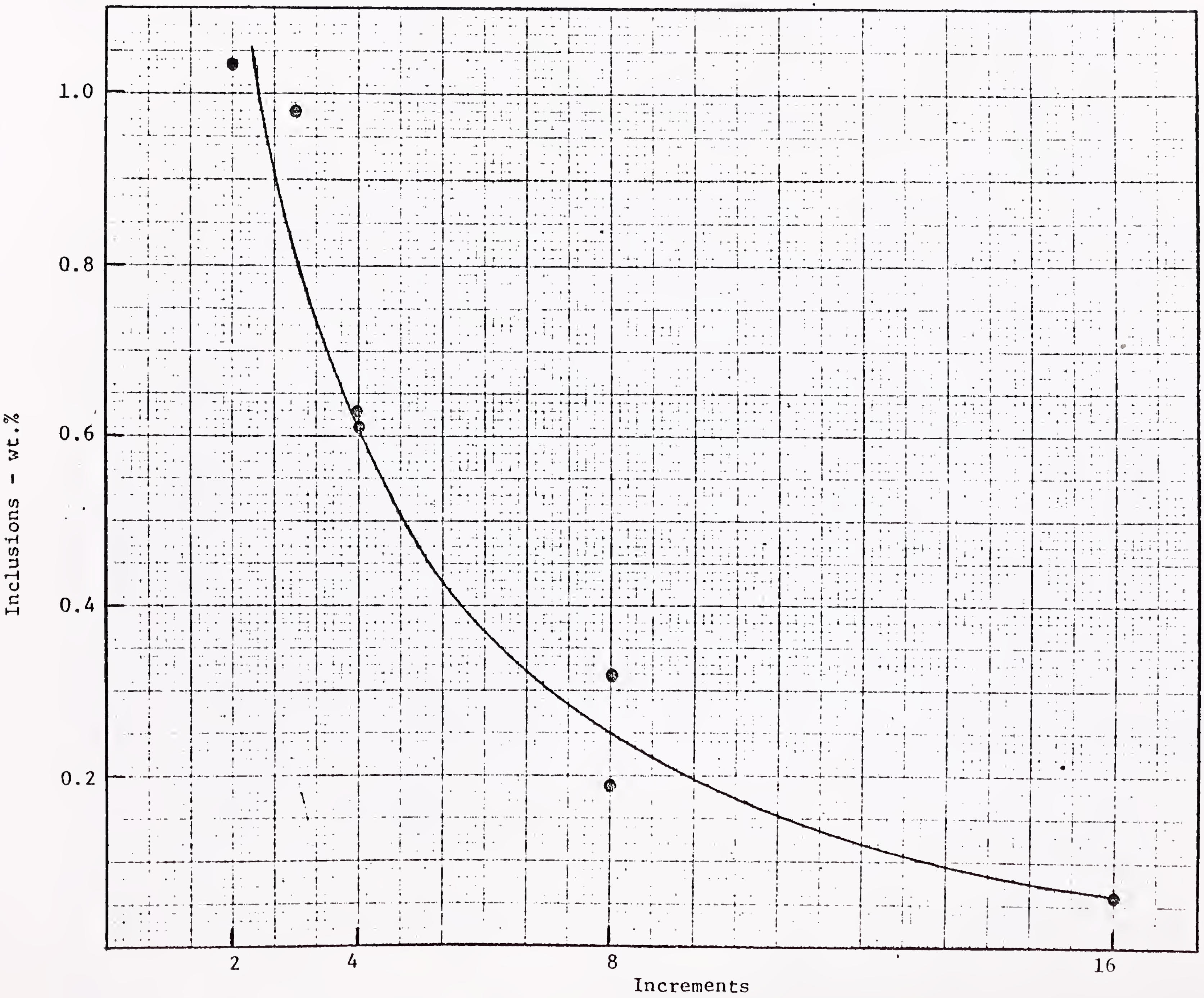


Figure 21. Weight percent of included SiC particles versus number of equal and equally spaced incremental additions of $TlNO_3$ for a sum total concentration of 1 g/1.

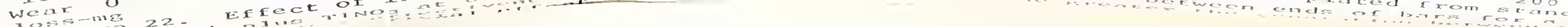


Figure 22. Effect of Tl at [illegible] plated from standard 400 g/1 CrO$_3$ bath plus TlNO$_3$ [illegible] between ends of bars for a given test [illegible]

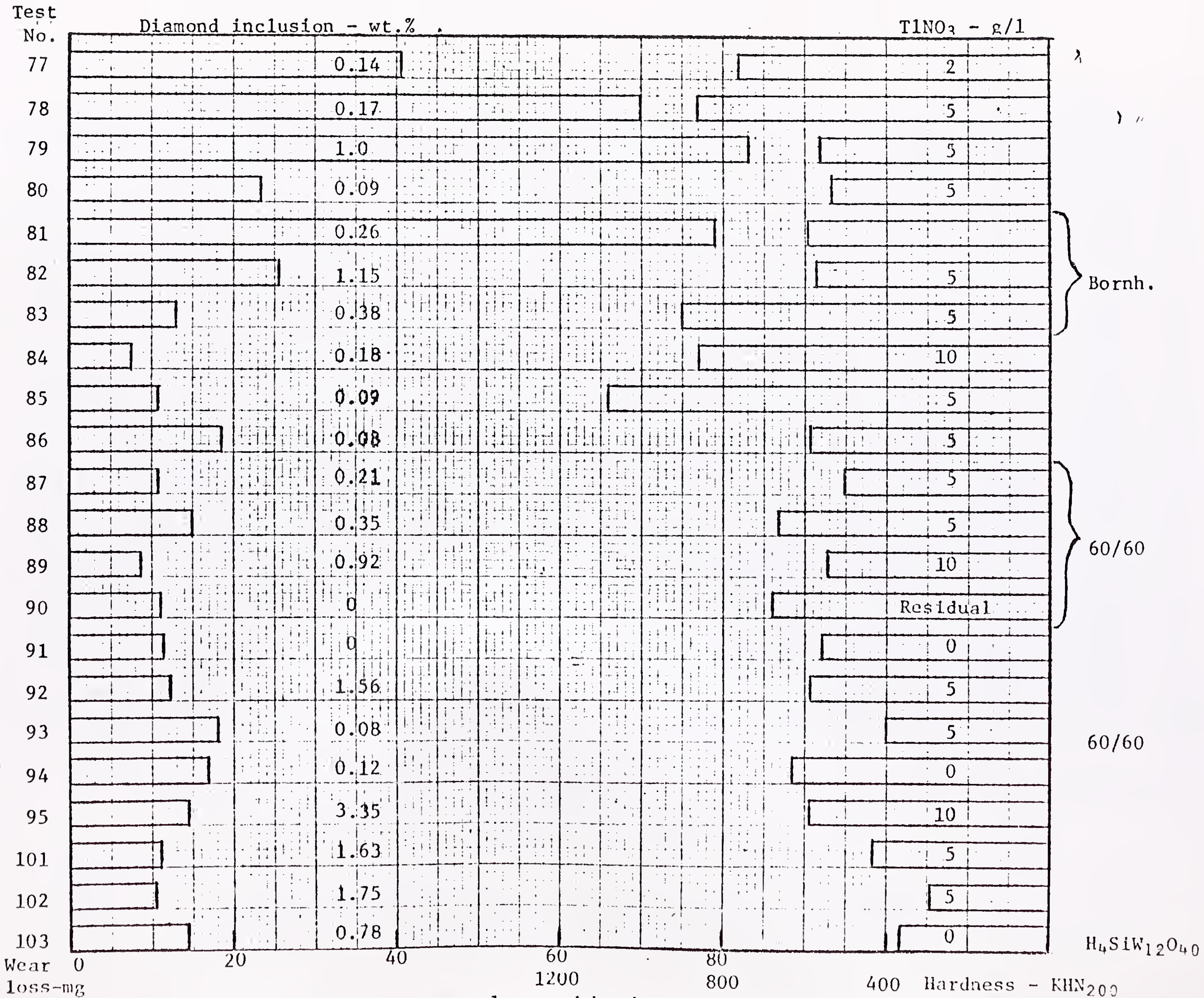


Figure 22. Effect of inclusions on wear loss and hardness of chromium deposits plated from standard 400 g/l CrO_3 bath plus $TlNO_3$ at 60°/40 asd, except as indicated. Distance between ends of bars for a given test roughly indicates effectiveness of inclusions in deposit, the greater the separation between the bar ends

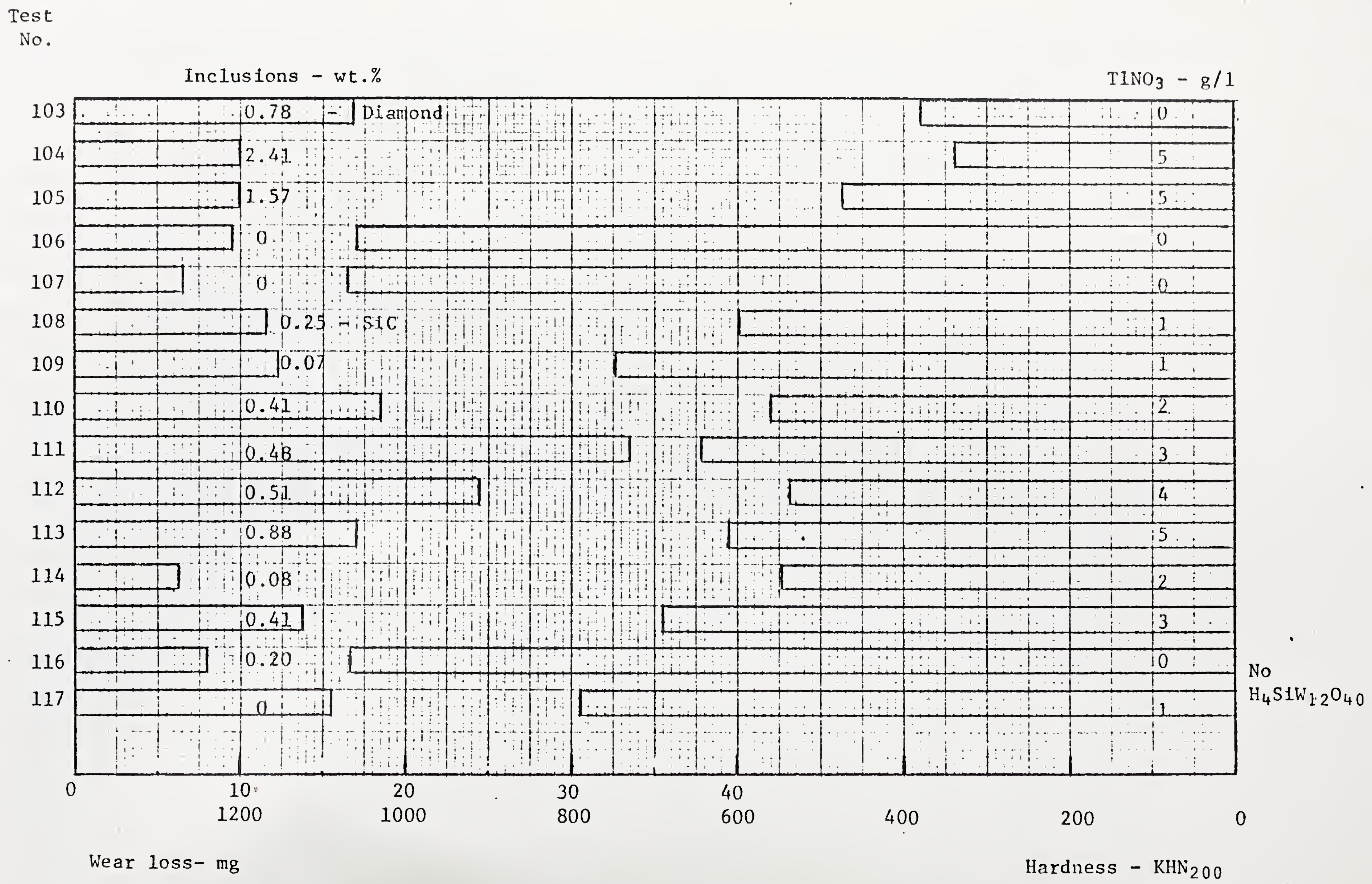


Figure 23. Wear loss in relation to hardness of deposits from standard 200 g/l CrO_3 bath plus $TlNO_3$ and 1-3 g/l $H_4SiW_{12}O_{40}$, except as indicated.

Wear loss – m

Figure 24. Wear plo

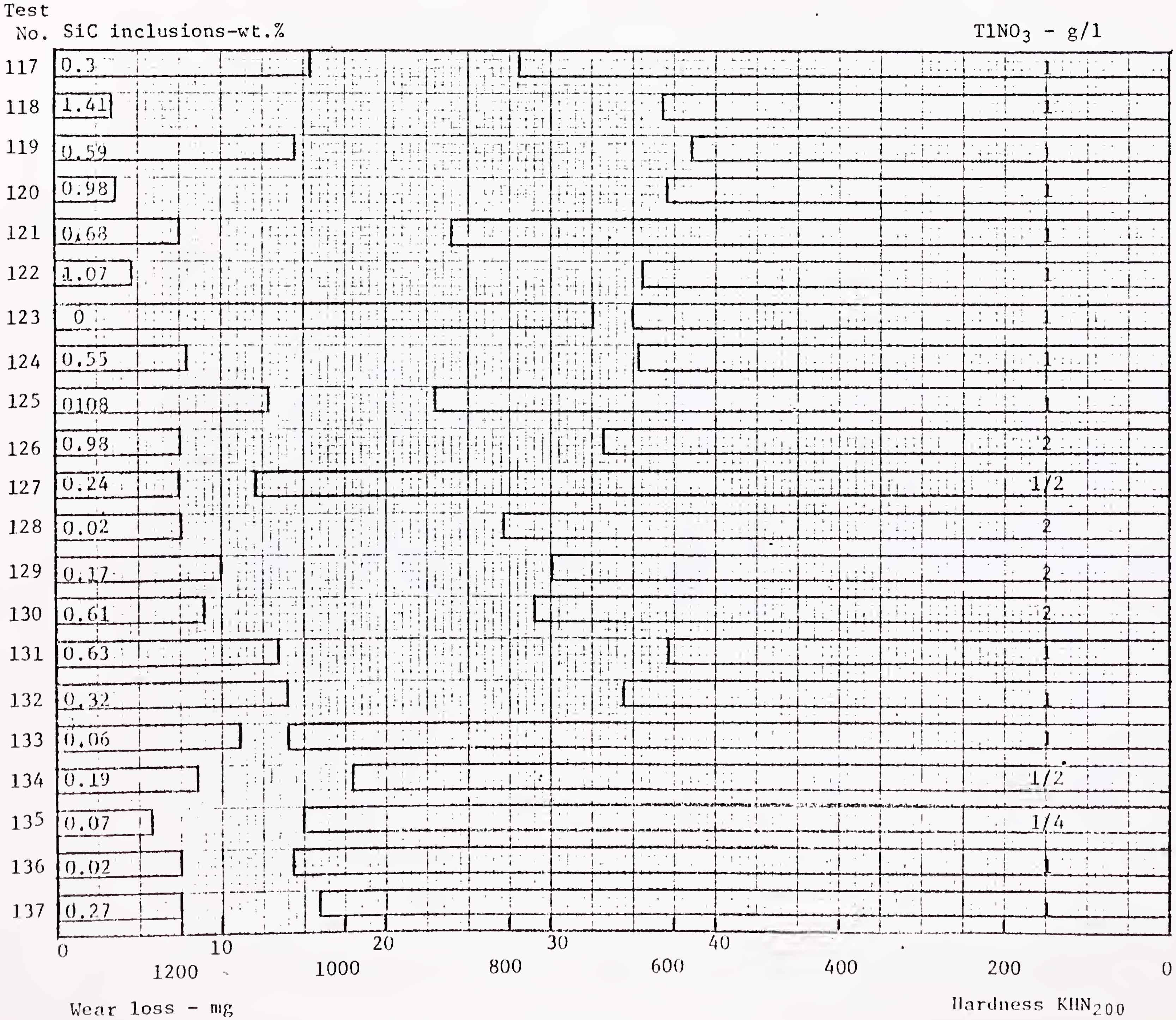


Figure 24. Wear loss in relation to hardness of deposits from standard 200 g/1 CrO_3 bath plus $TlNO_3$ and SiC.

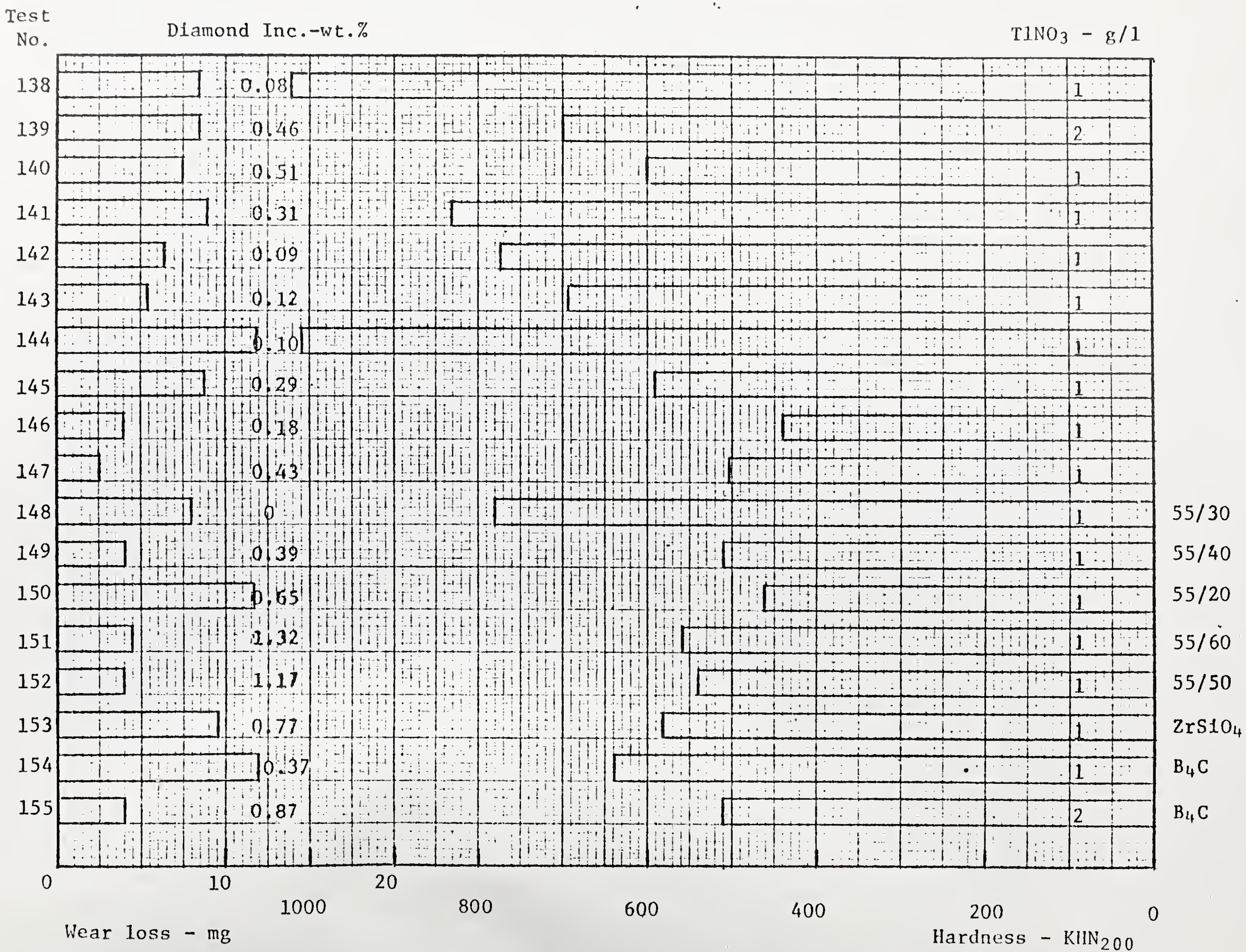


Figure 25. Wear loss in relation to hardness of deposits from standard 200 g/1 CrO_3 bath plus $TlNO_3$ and diamond powder and at 55°/50 asd, except as otherwise indicated.

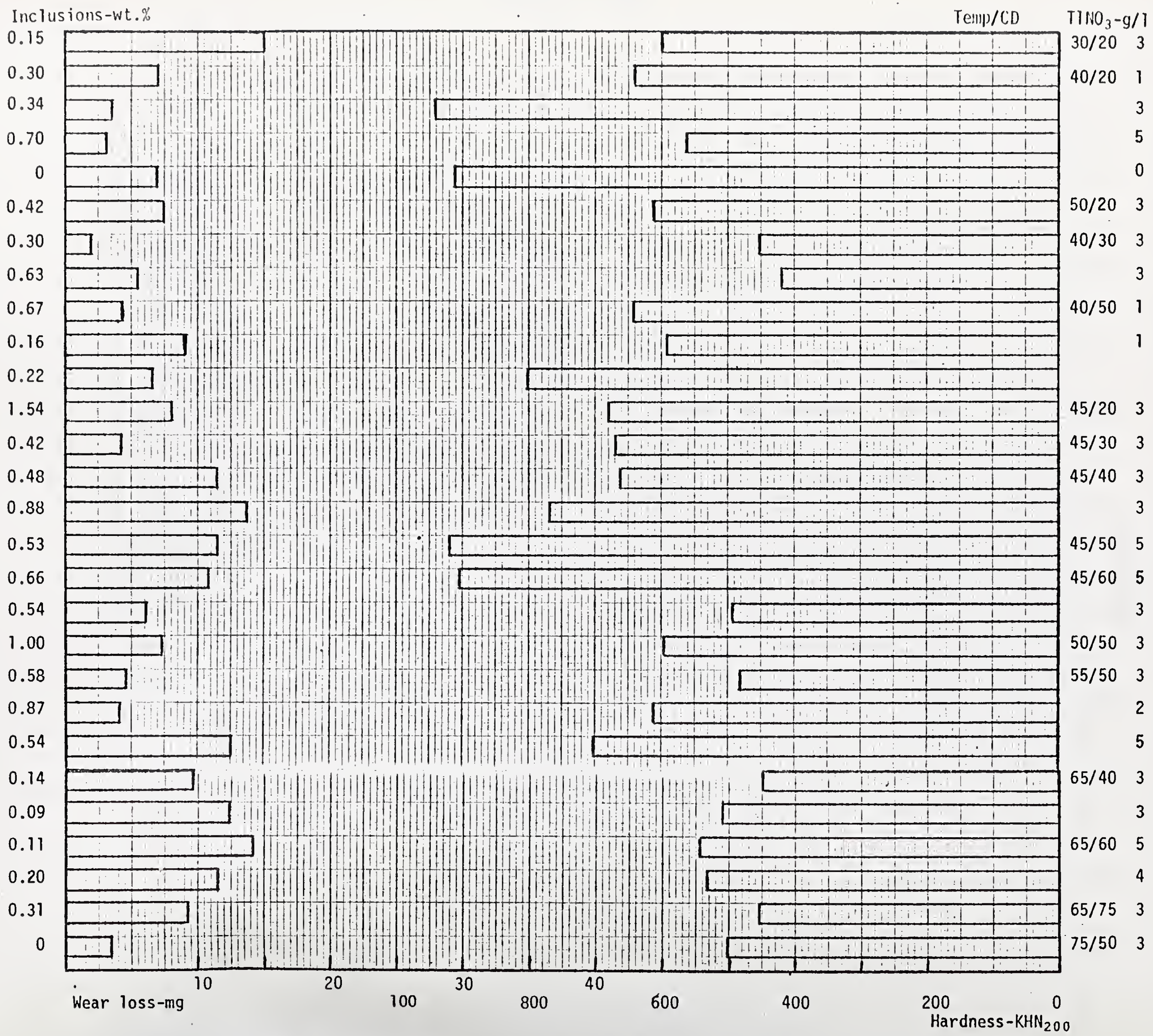


Figure 26. Summary of data on deposits with included material for several plating conditions with 30 g/l B_4C in the Cr bath.

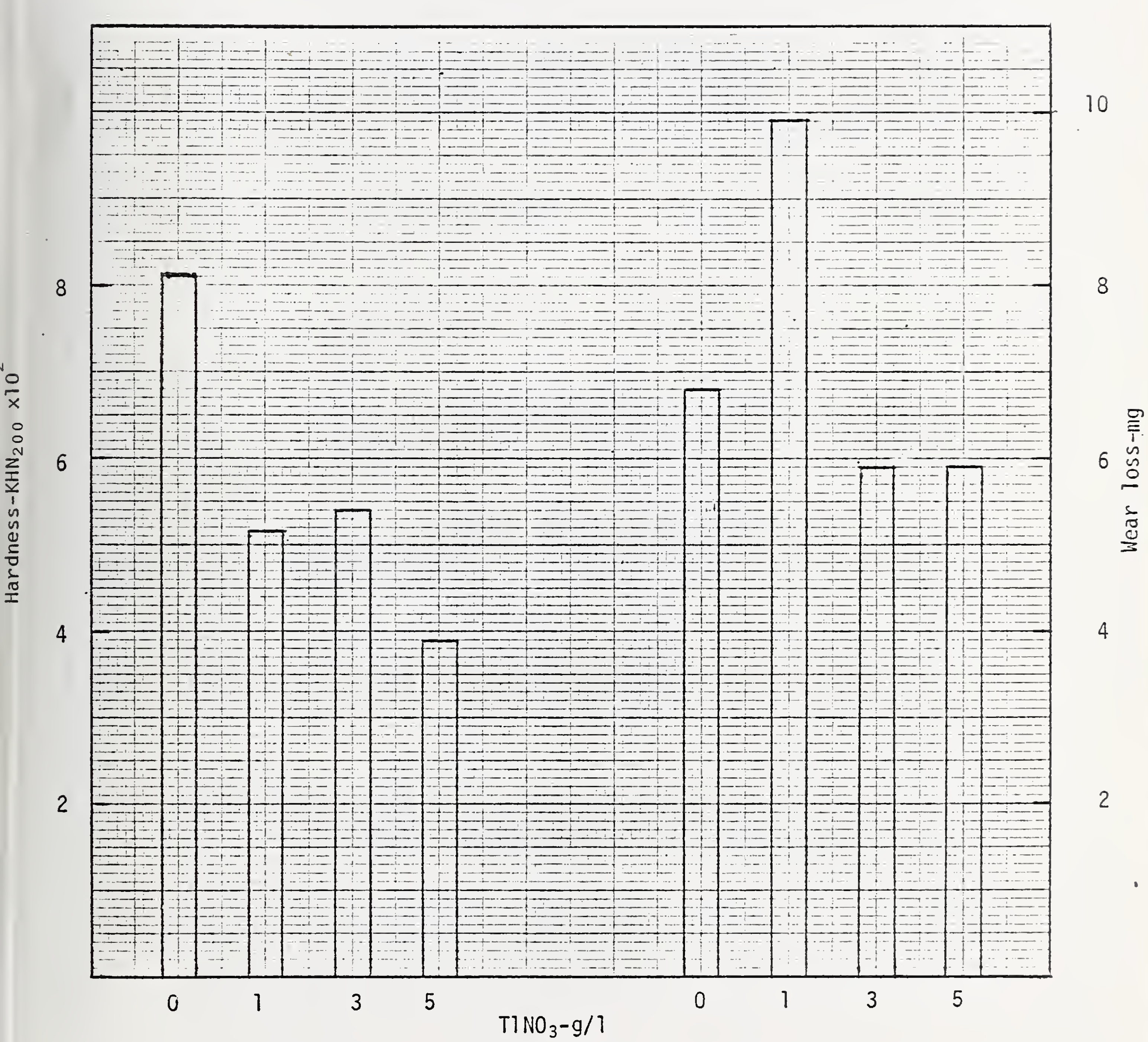


Figure 27. Effect of Tl concentration on wear and hardness at 40°/20 asd. No particles added to bath.

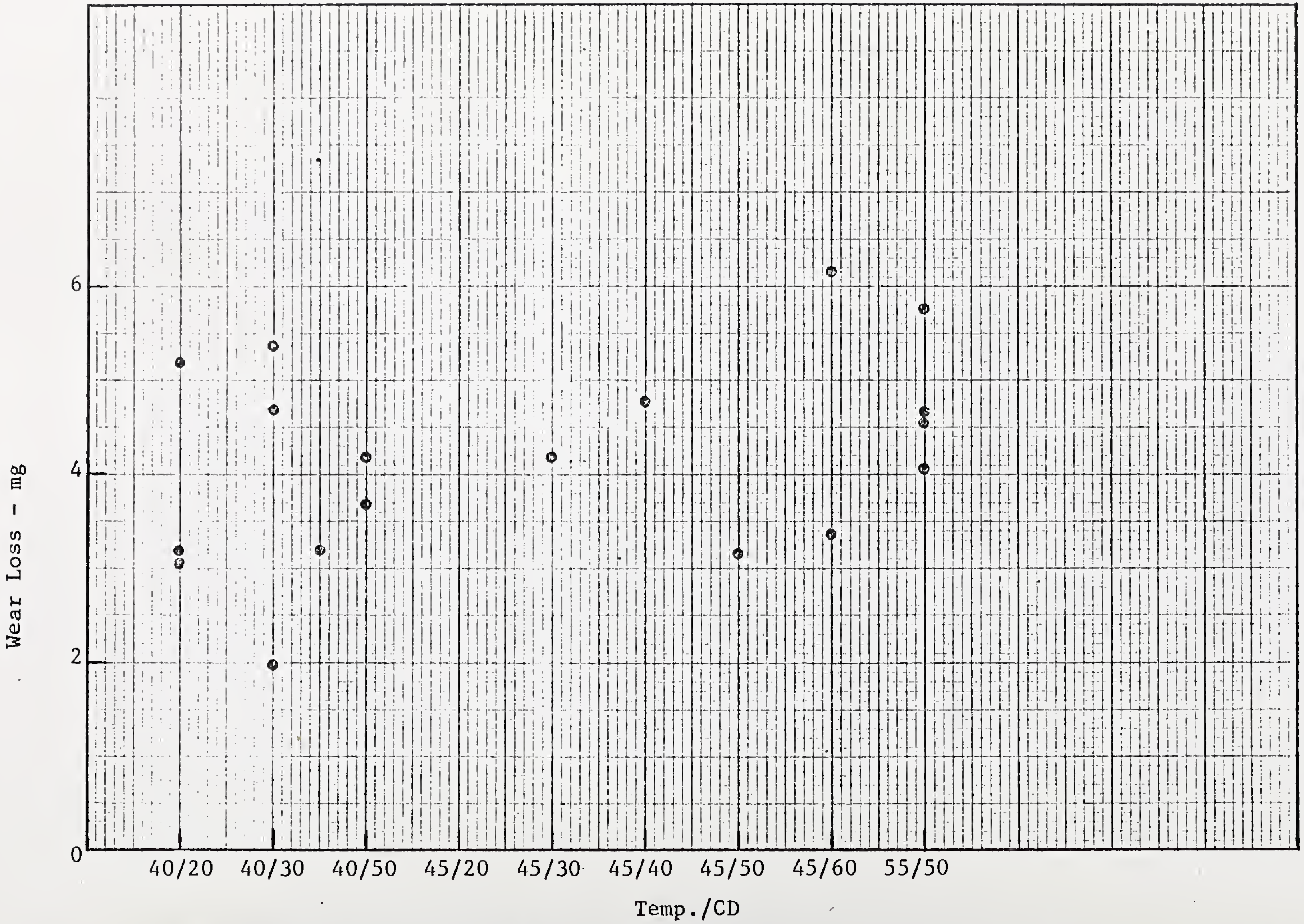


Figure 28. Temperature-Current Density for deposits with good wear resistance made with 30 g/l B_4C in plating bath. (Not all deposits plated at these conditions had wear characteristics equally as good.)

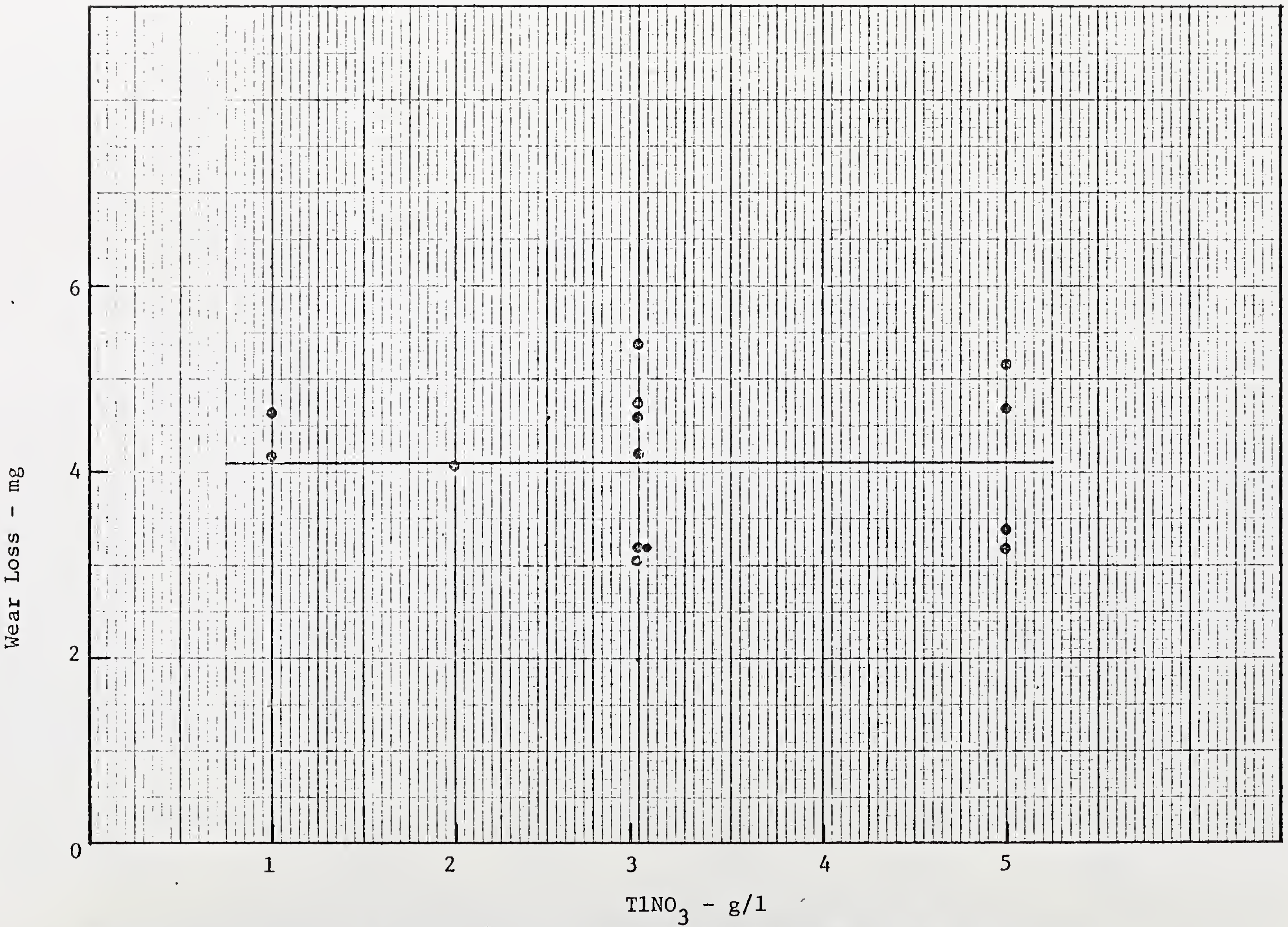


Figure 29. Wear versus Tl conc. for deposits with wear loss below 6 mg. Plated with 30 g/1 B_4C in bath. (Not all deposits plated at these conditions had wear characteristics equally as good.)

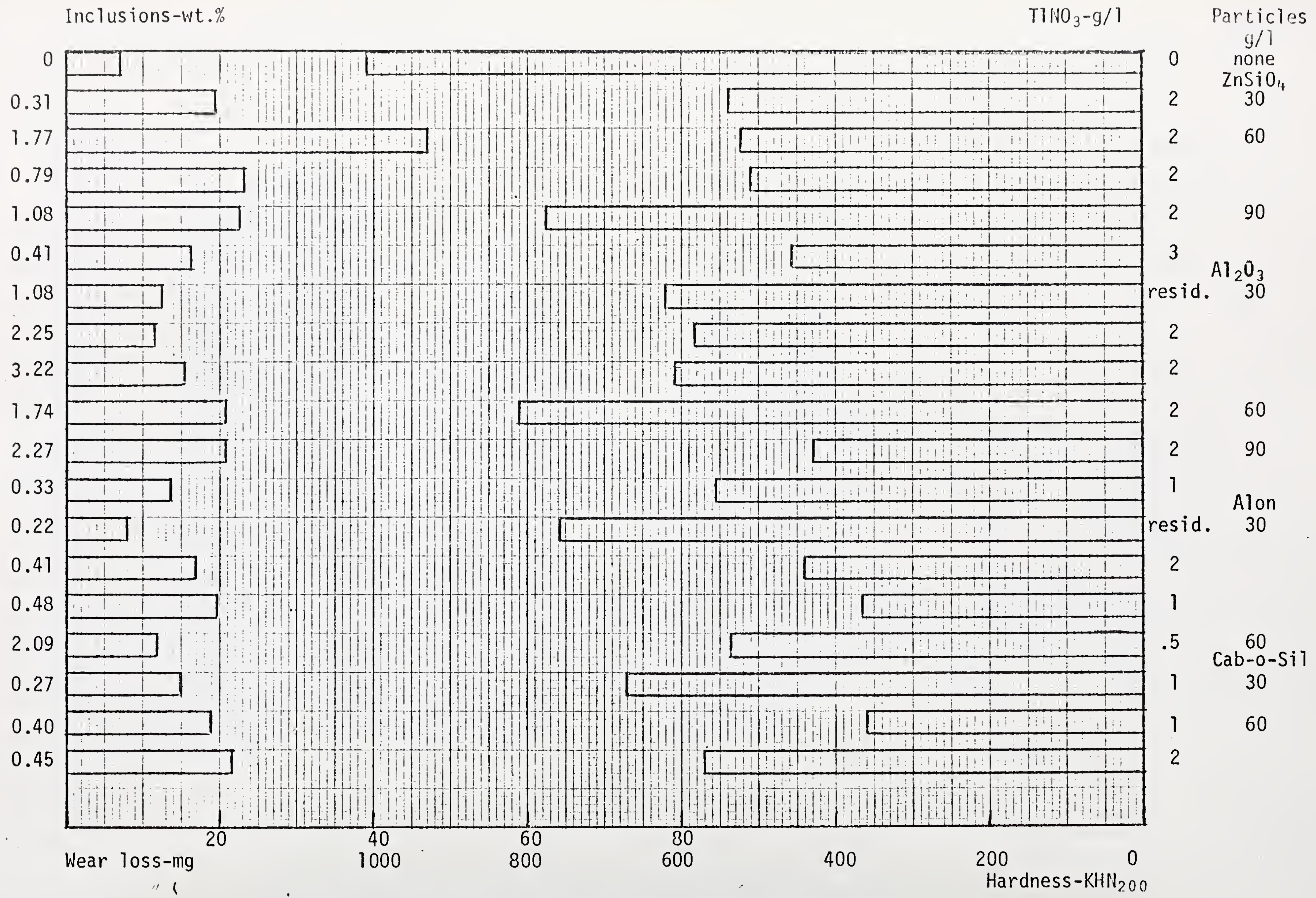


Figure 30. Summary of test deposits with new types of particles. Most runs at 45°/30 asd.

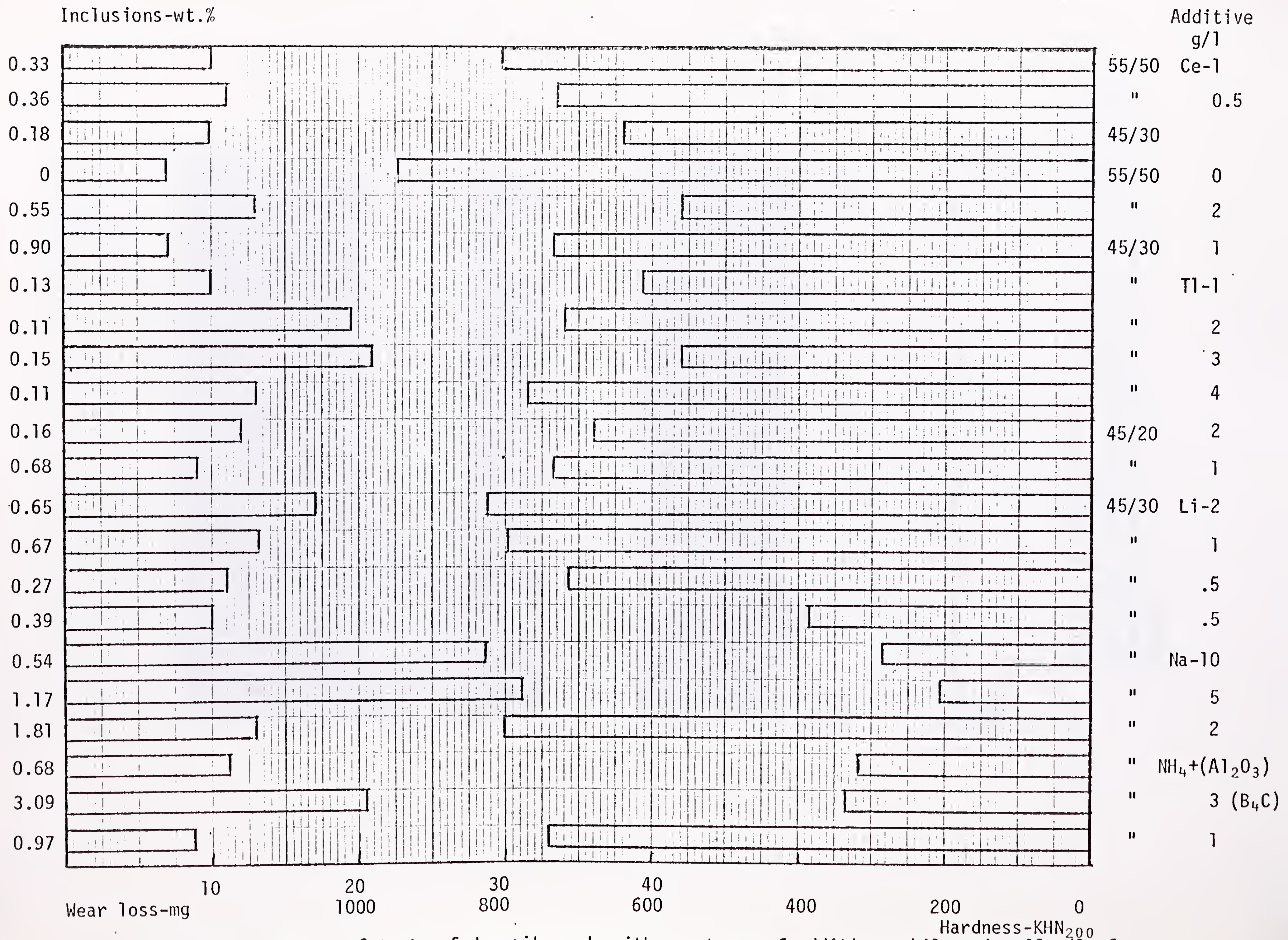


Figure 31. Summary of tests of deposits made with new types of additives while using 30 g/l of SiC in the bath.

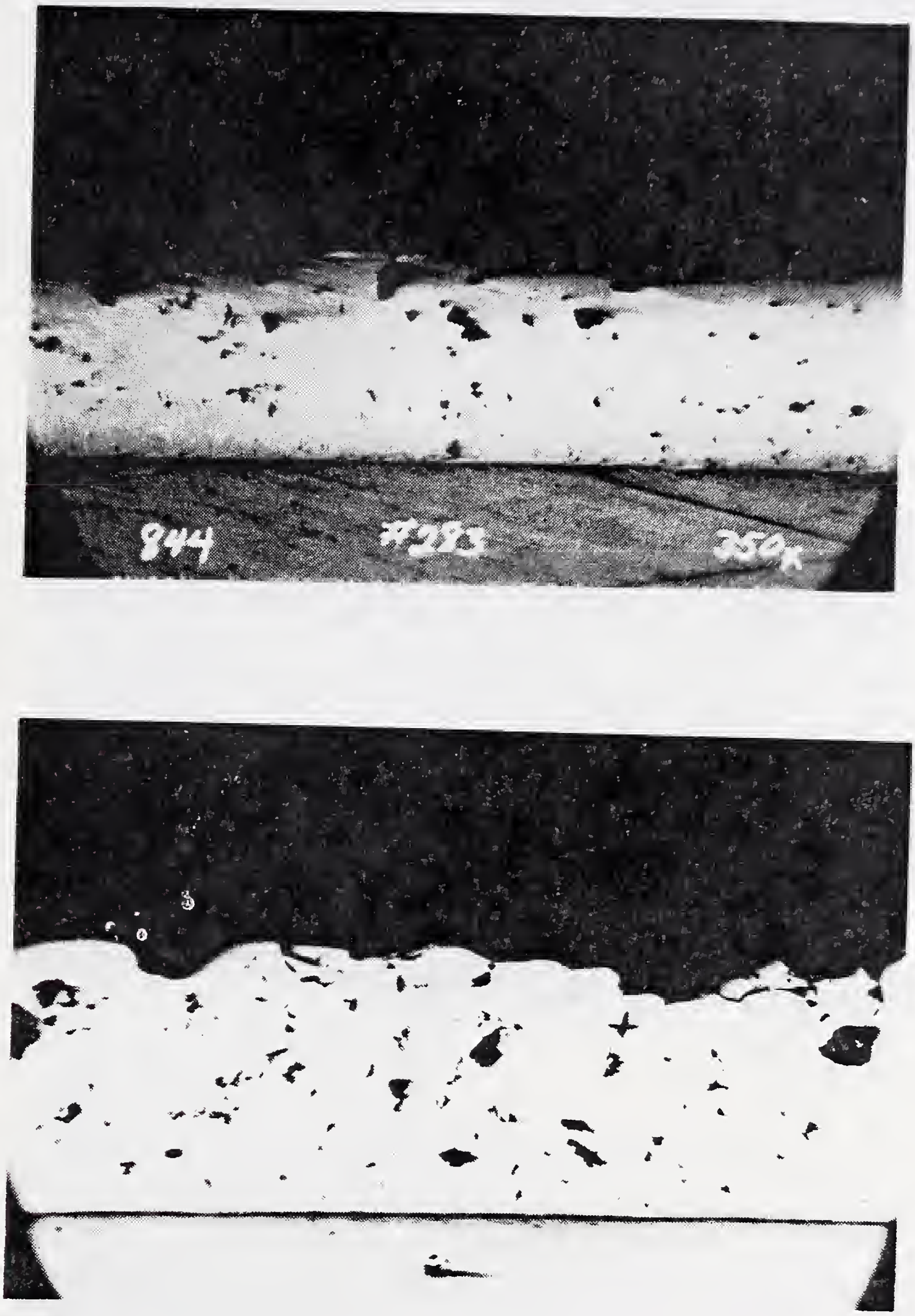


Figure 32. Deposits made under similar conditions using 1 g/l $CeNO_3$ (top) and 1 g/l $TlNO_3$. Note the lesser distortion (large dark areas, roughness and fissures) of the chromium structures by the $CeNO_3$ for roughly similar amounts of included material.

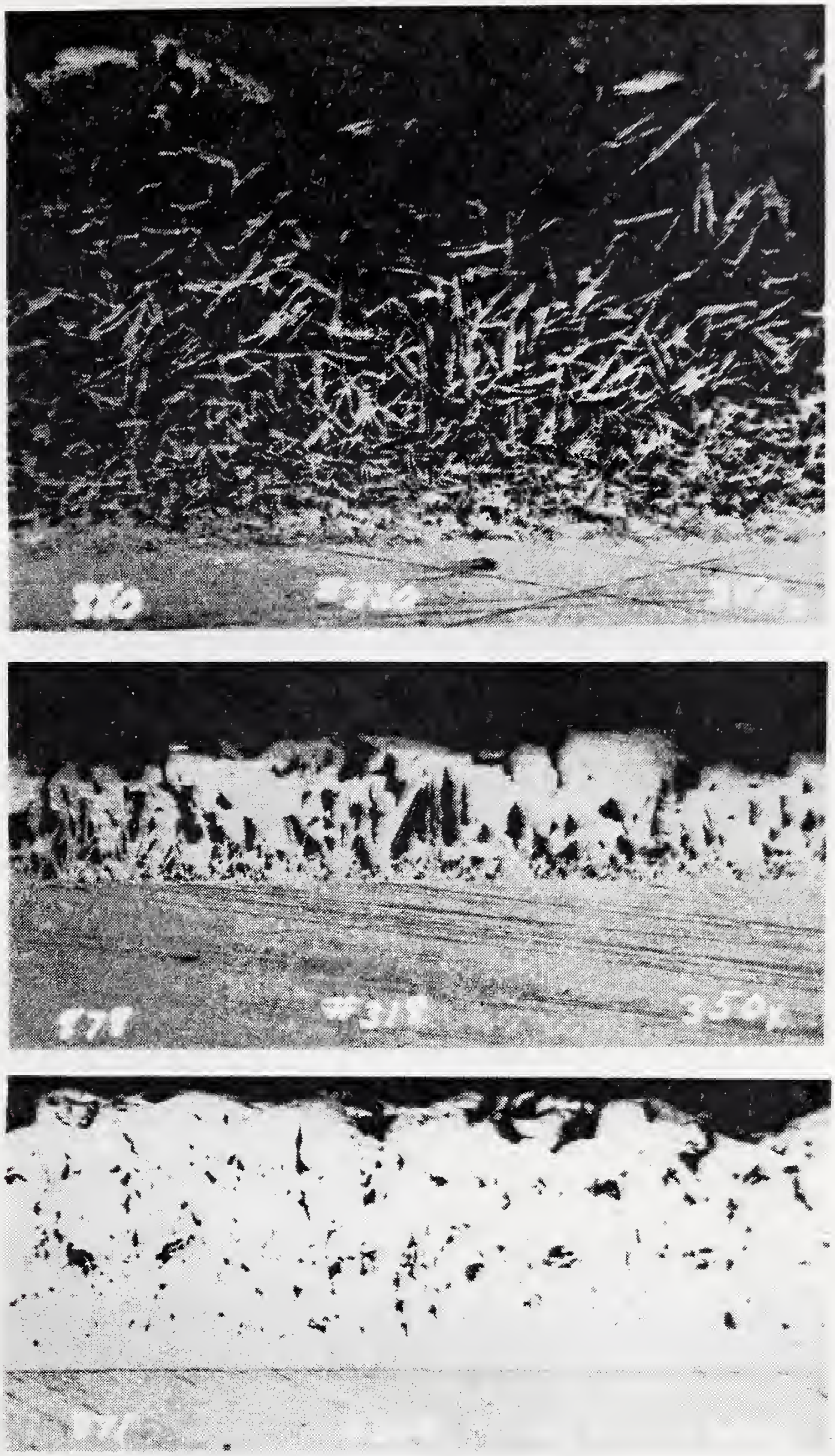


Figure 33. Comparison of effect on structure of 5 g/l $LiNO_3$ (top), about 4 g/l NH_4NO_3 (center), and 5 g/l $TlNO_3$. Wear for the deposits would be less than for standard chromium. Appreciable inclusions were contained in all, but were loosely held in the discontinuities rather than firmly anchored in the chromium matrix.

Figure 34. Comparison of structure of deposits at 1 g/l (top) and 1/2 g/l $NaNO_3$ additive in plating bath. Roughly the same amount of SiC particles (0.3-0.4 wt.%) were included in each deposit. Some of the larger dark areas in the top photo are considered to be discontinuities in the chromium rather than inclusions.

Figure 35. Chromium plated on a vertical surface with included silicon carbide (0.45 wt.%) from a bath containing 2 g/l $CeNO_3$. For comparison to a roughly equivalent horizontal deposit, see top photo in Figure 7.

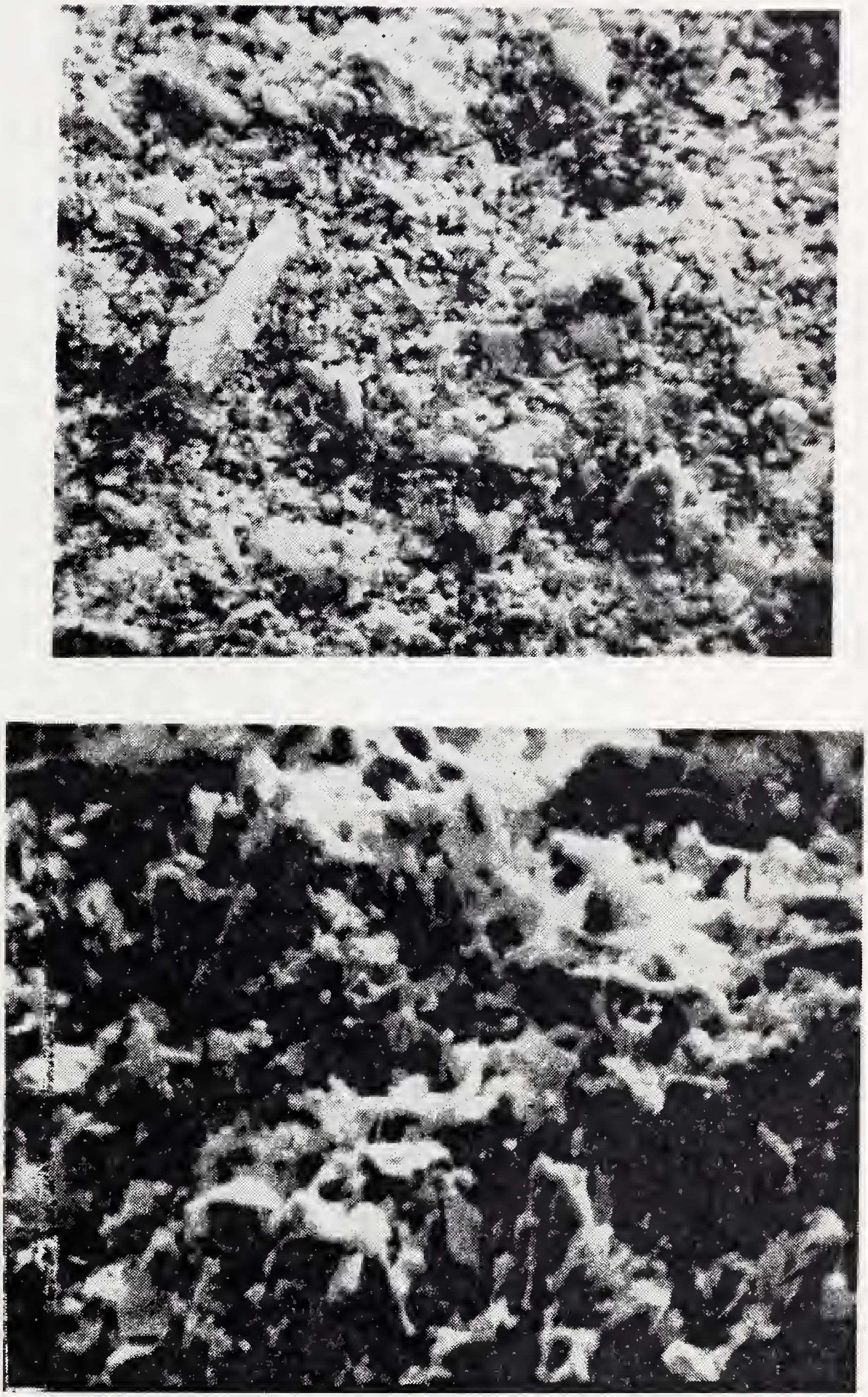


Figure 36. SEM photos of B_4C (top) and B_6C hard particles at about 1600X.

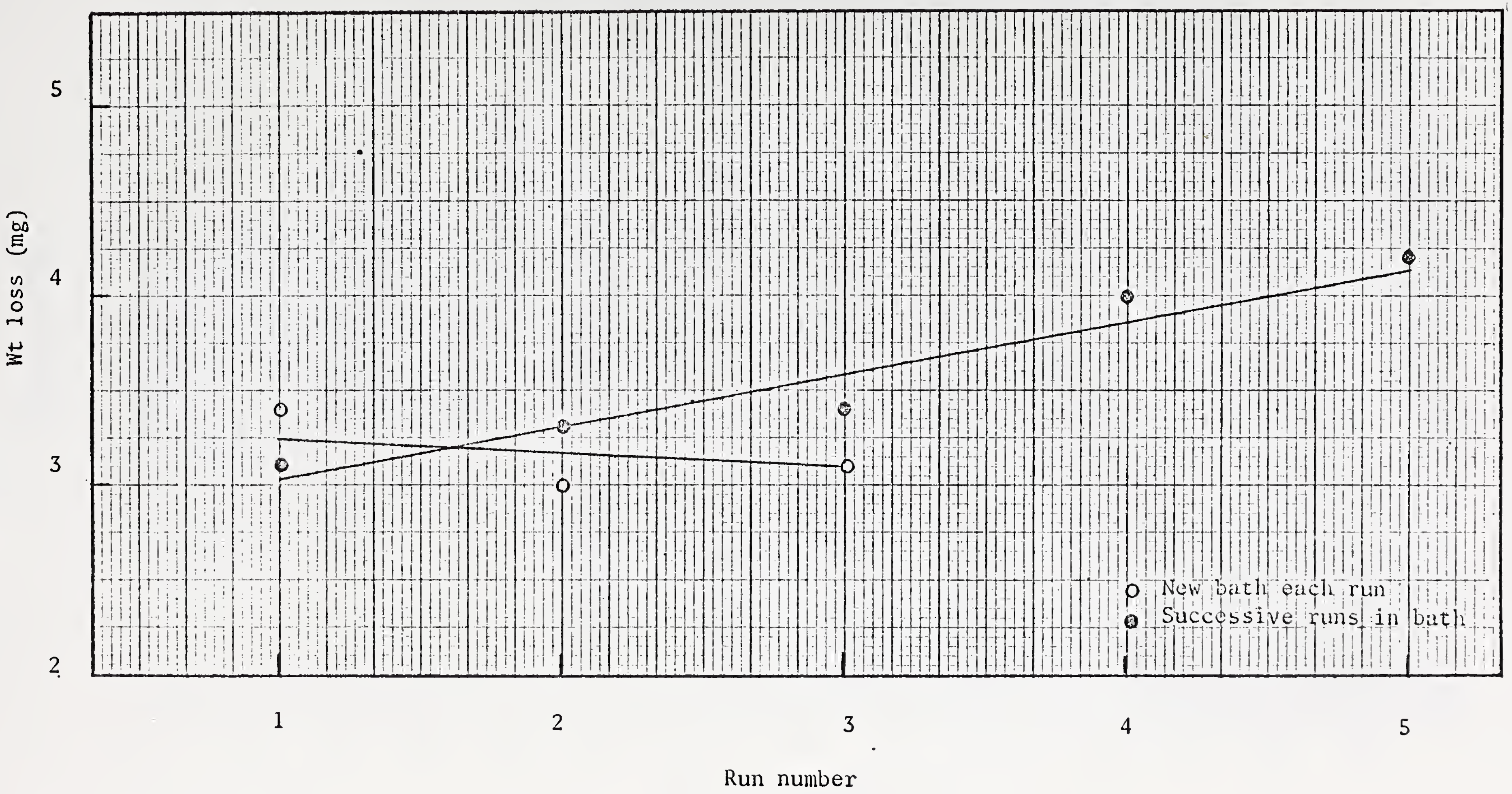


Figure 37. Bath aging effect on wear of deposits plated in a bath containing 3 g/l $TlNO_3$ and 30 g/l B_4C at 45°/30 asd.

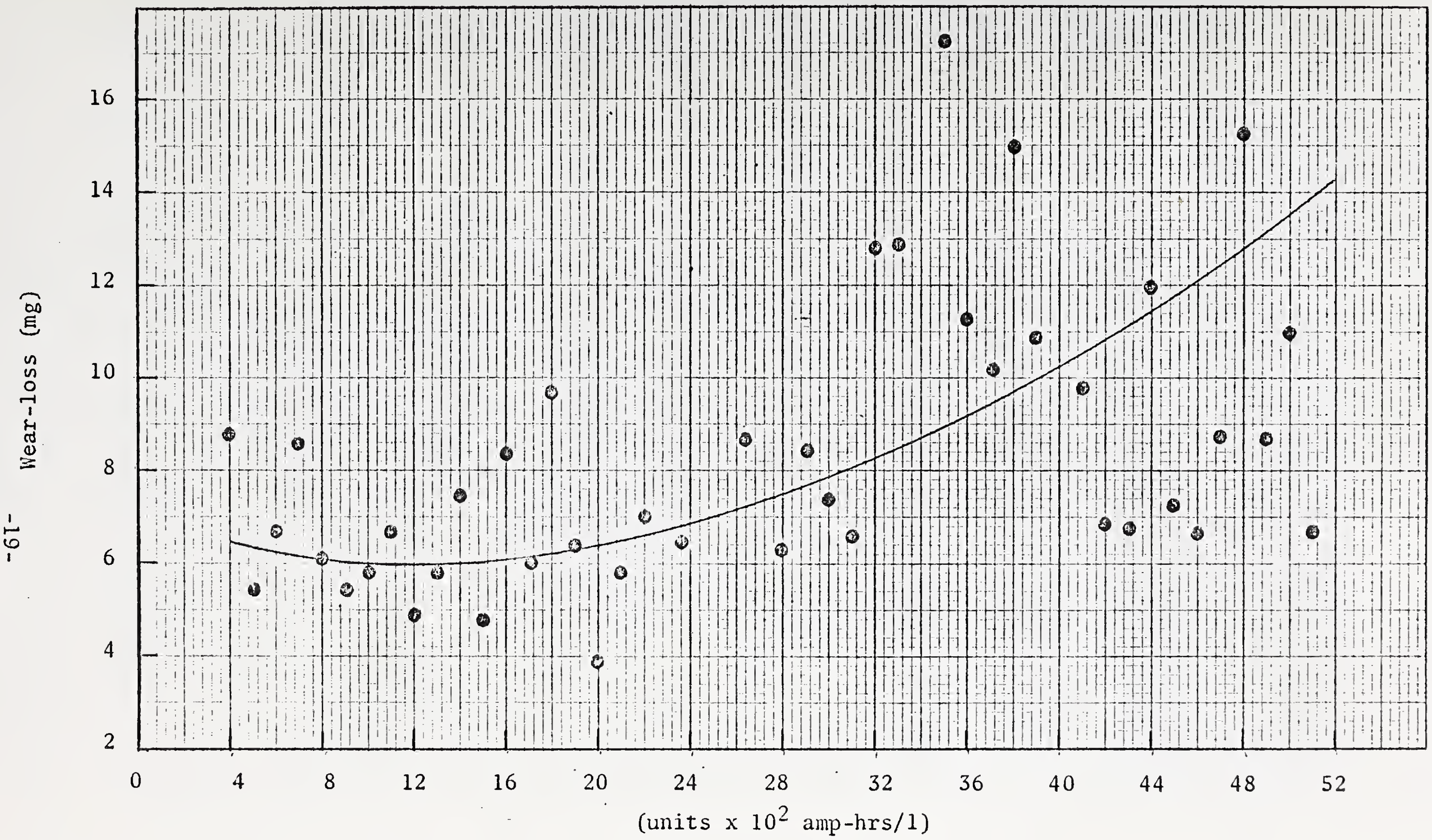


Figure 38. Bath-life test using mainly NH_4NO_3 as an additive at plating conditions of 45°C/20 asd to 55/50.

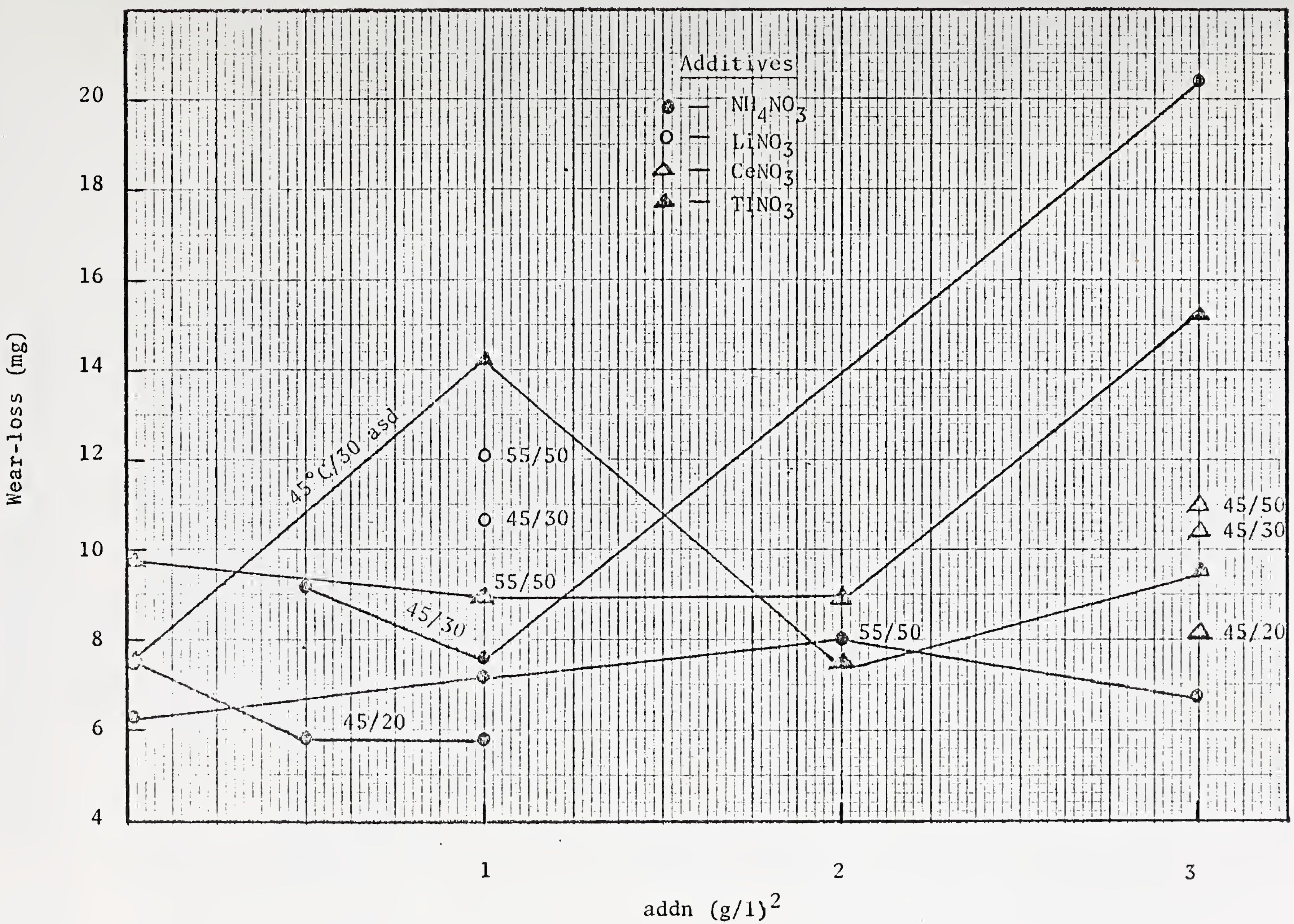


Figure 39. Performance of various additives used in 200 g/1 CrO_3 bath with suspended particles.

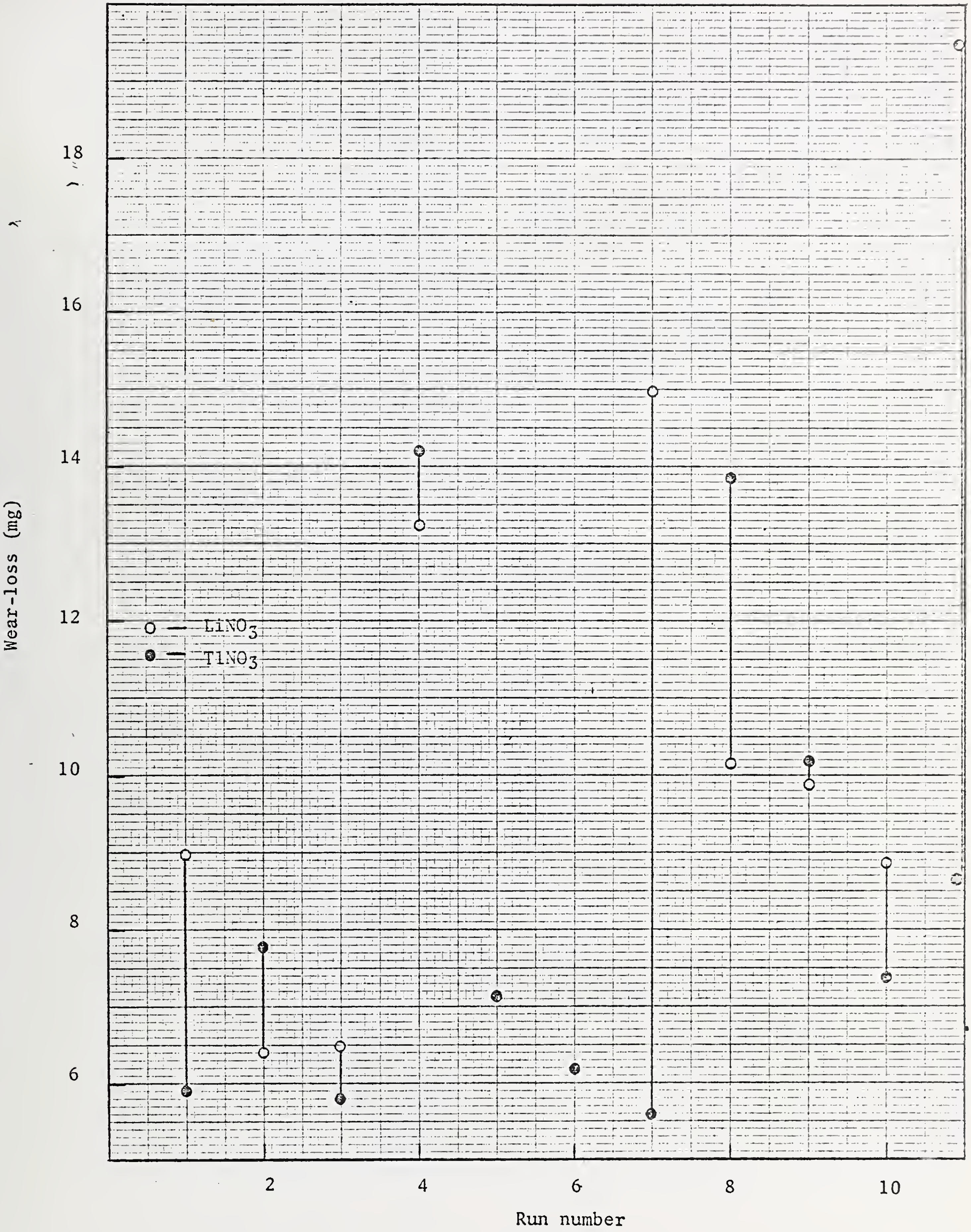


Figure 40. Comparison of effect of bath additives under similar plating conditions.

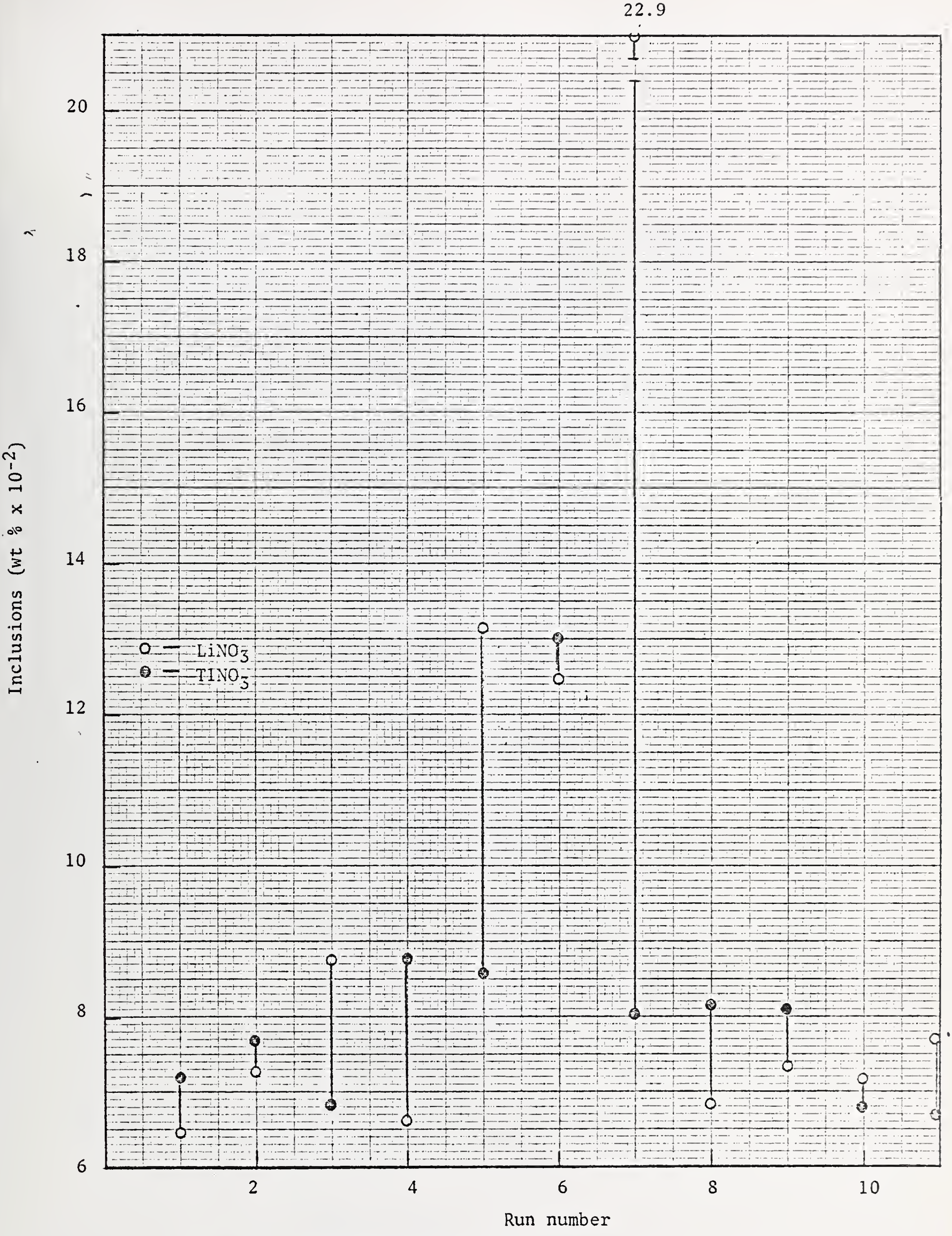


Figure 41. Comparison of effect of additives to Cr bath under similar plating conditions.

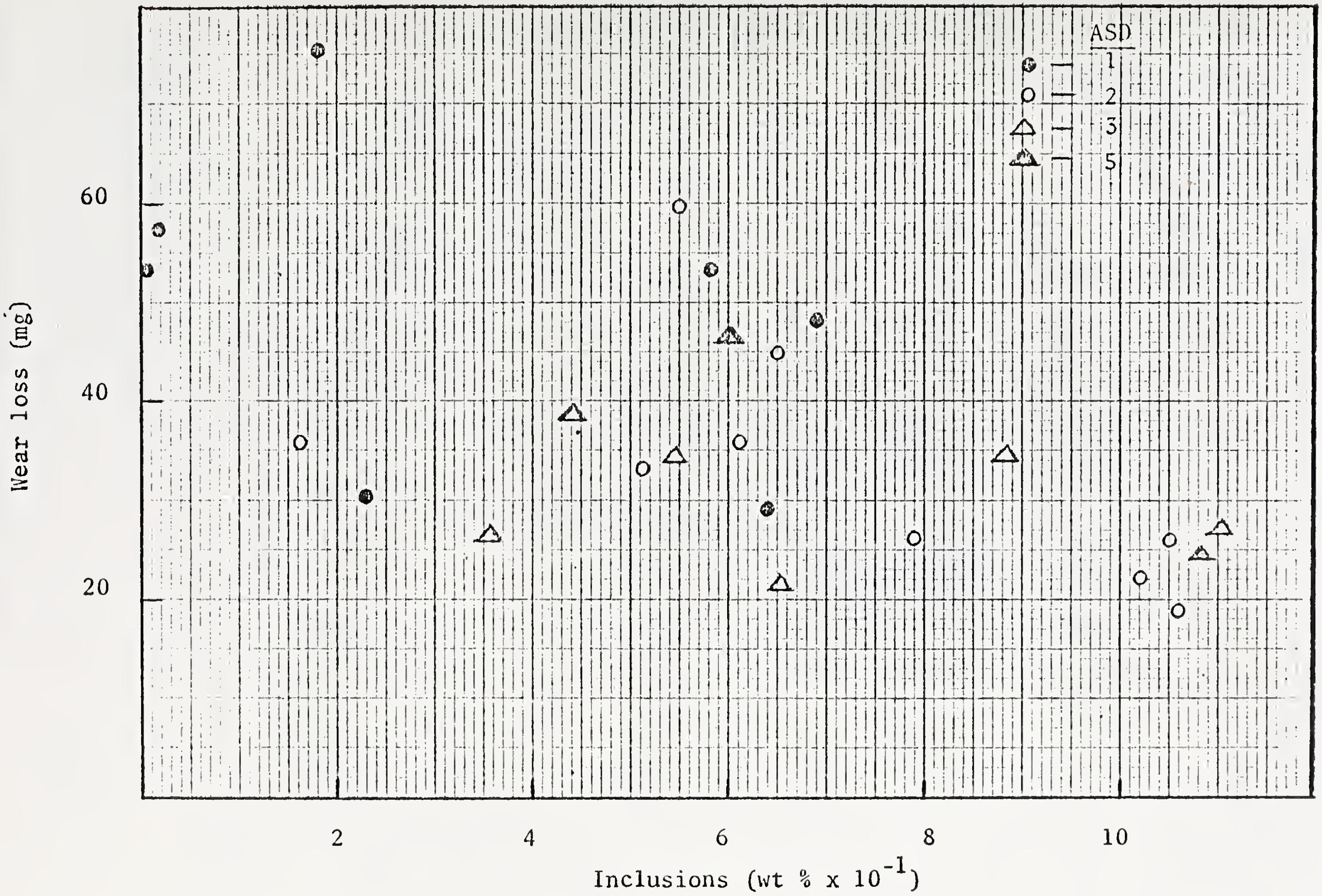
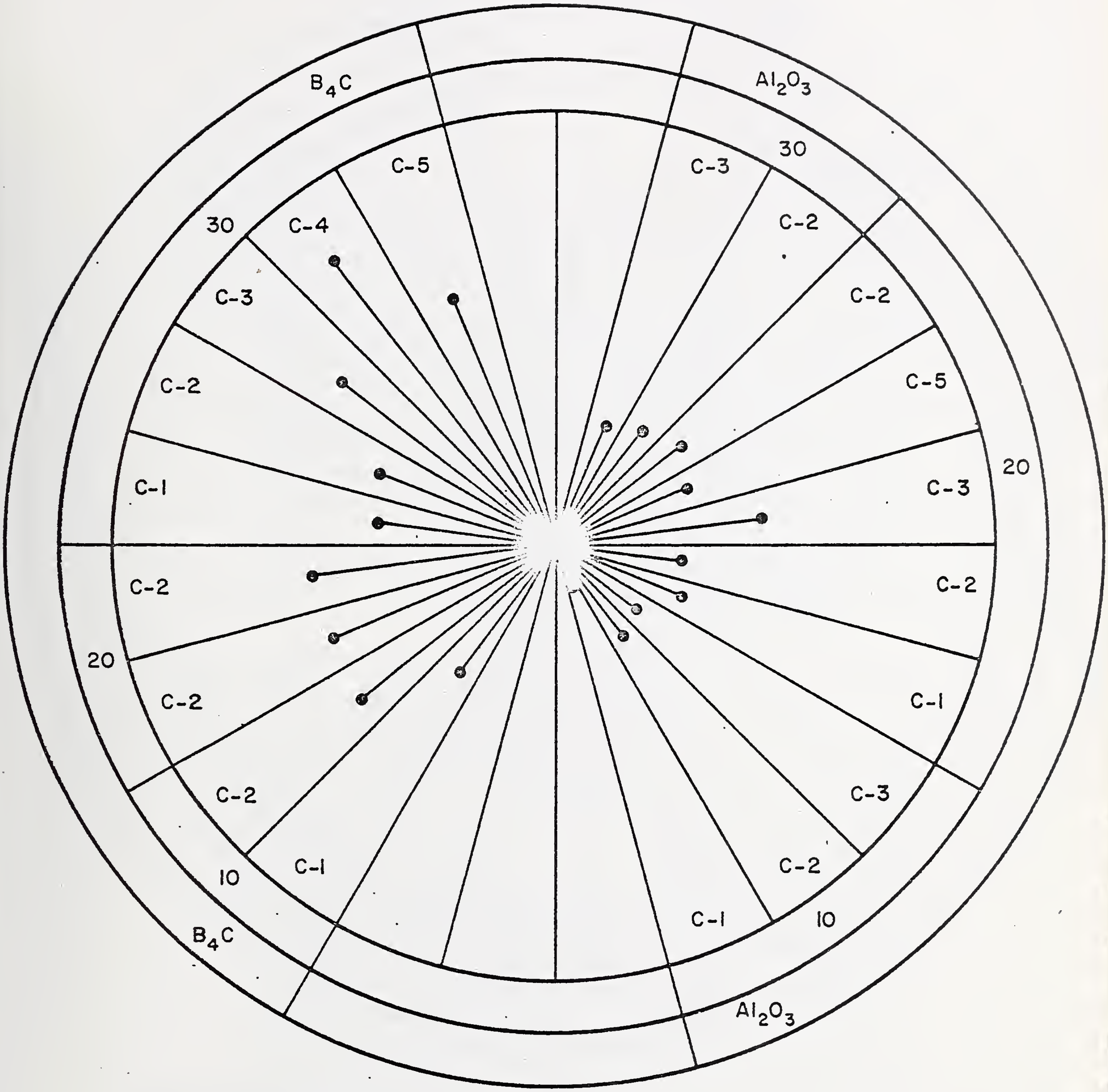
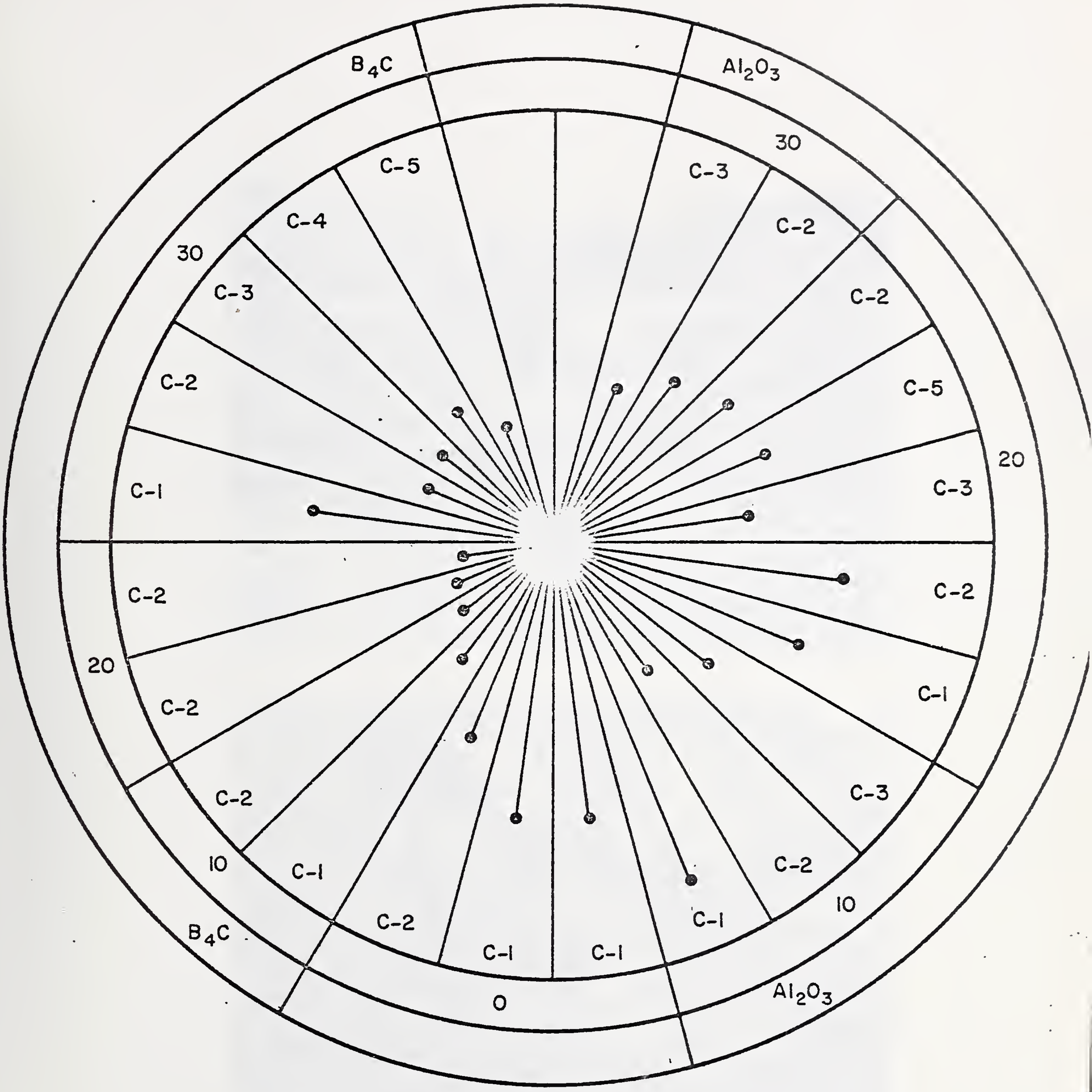


Figure 42. Inclusions versus wear in Cd plated at 24°C in CN bath.



Temp. = 24°C
C = Current density in asd
Inside ring = g/1 particles in bath
Radii = Inclusions 0.3 wt. %

Figure 43. Amount of inclusions in cadmium deposits.



Temp. = 34°C
C = Current density in asd
Inside ring = g/1 particles in bath
Radii = Wear loss 15 mg

Figure 44. Wear-loss of cadmium deposits with included particles.

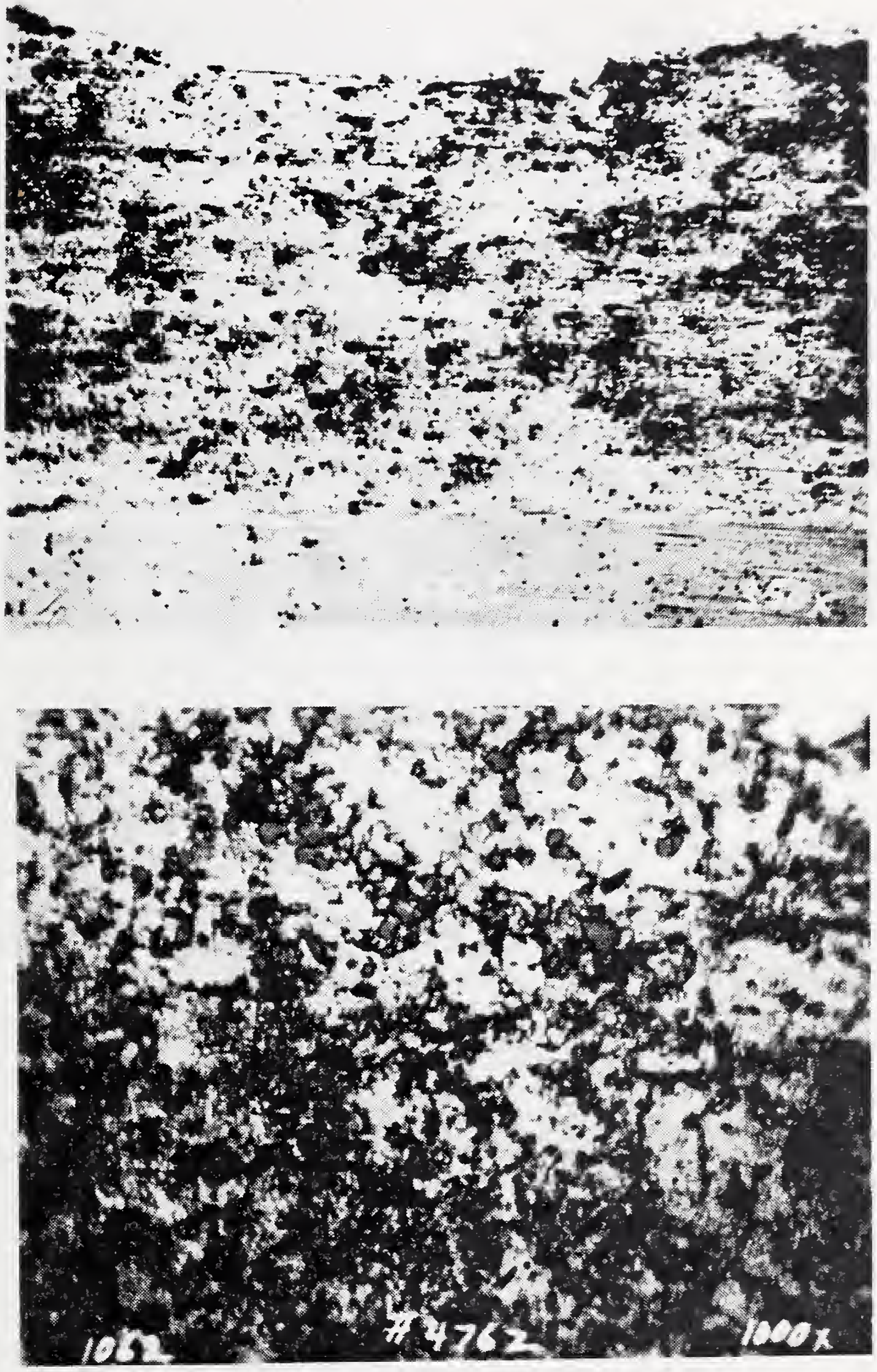


Figure 45. Cadmium (top) and zinc deposits containing B_4C particles plated from cyanide baths at 24°C/1 and 3 asd respectively. No etch.

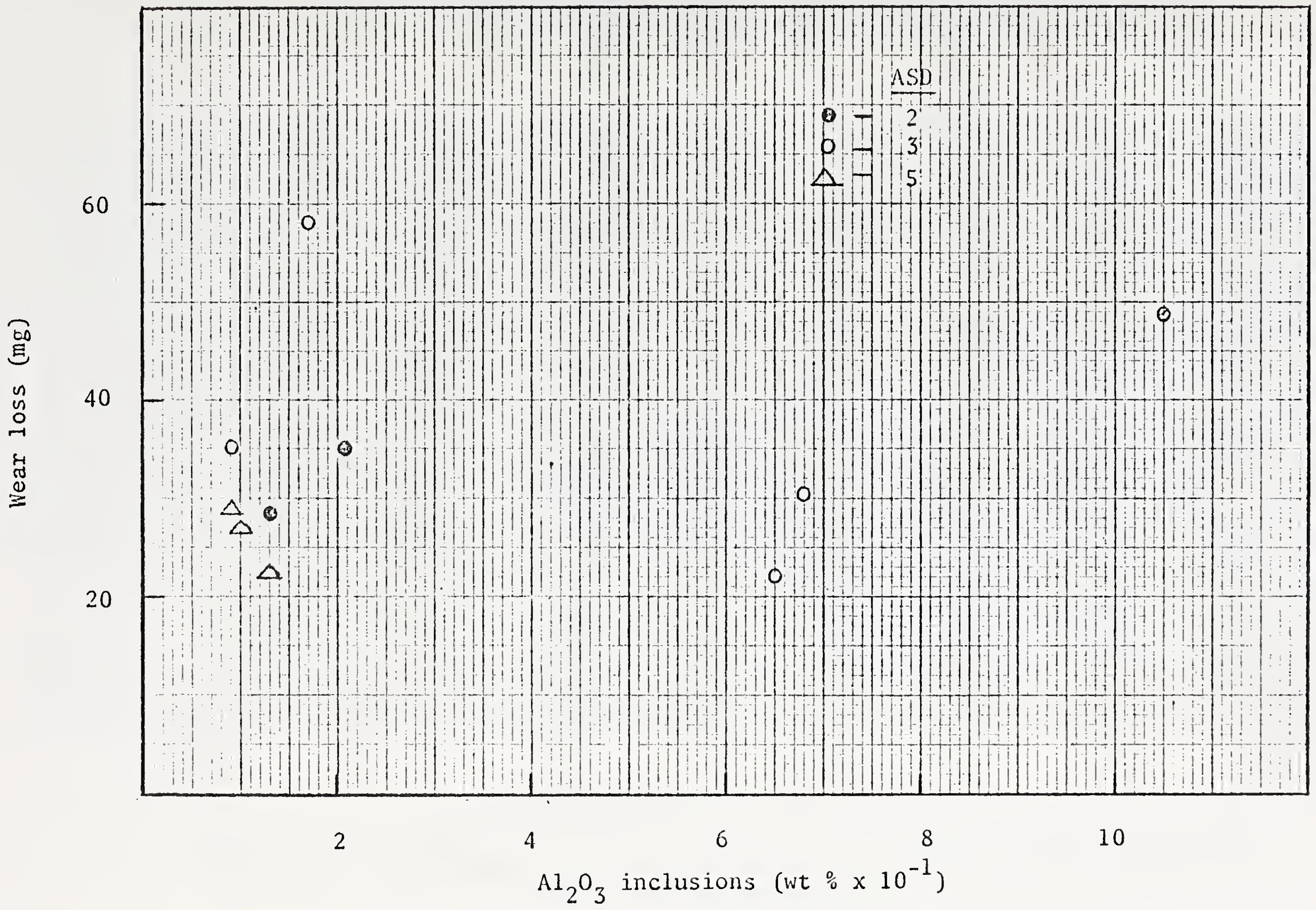


Figure 46. Inclusions versus wear-loss for zinc with included Al_2O_3 deposited in a cyanide bath at 24°C.

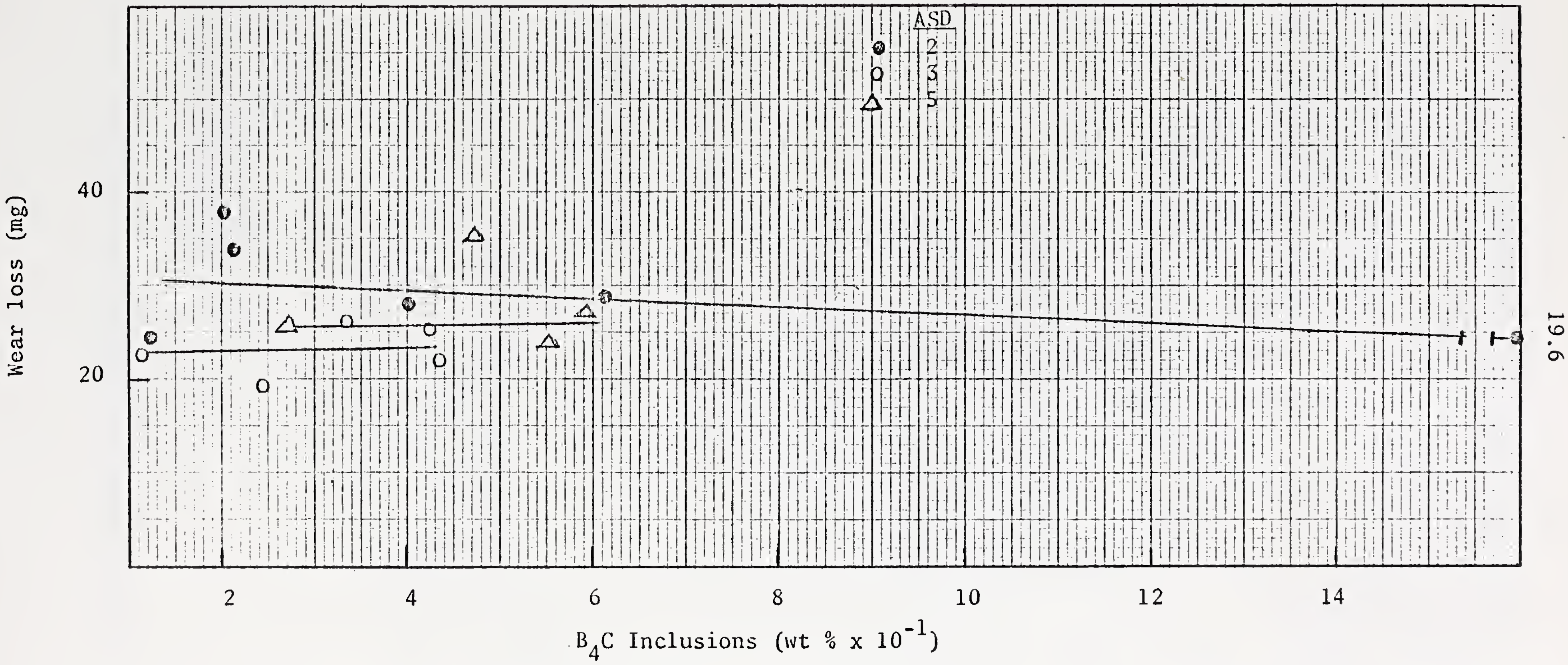
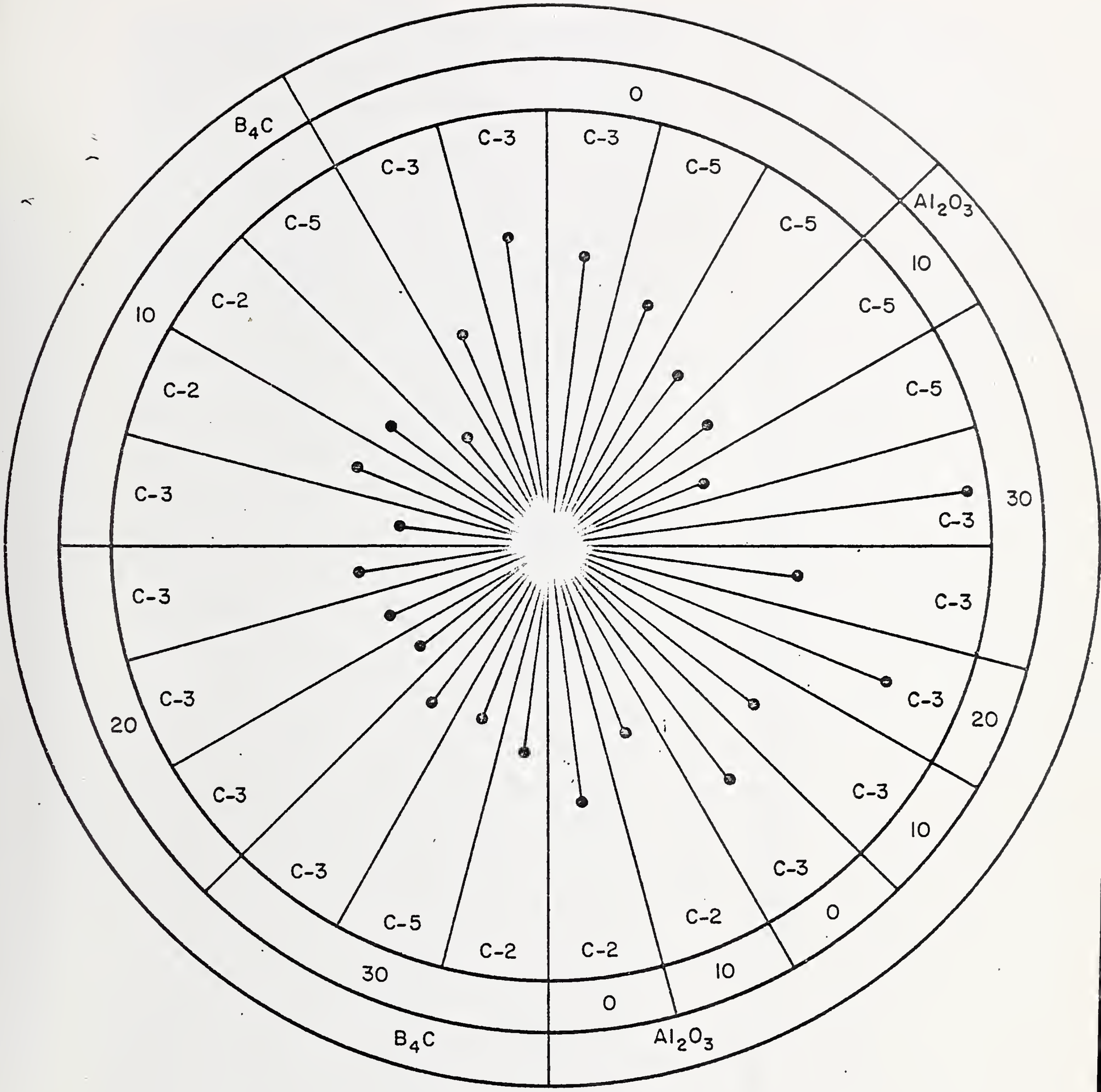


Figure 47. Inclusions versus wear-loss for zinc deposits with included B_4C from a cyanide bath at 24°C.



Temp. = 24°C
C = Current density in asd
Inside ring = g/1 particles in bath
Radii = Wear loss

Figure 48. Wear-loss of zinc deposits with included particles.

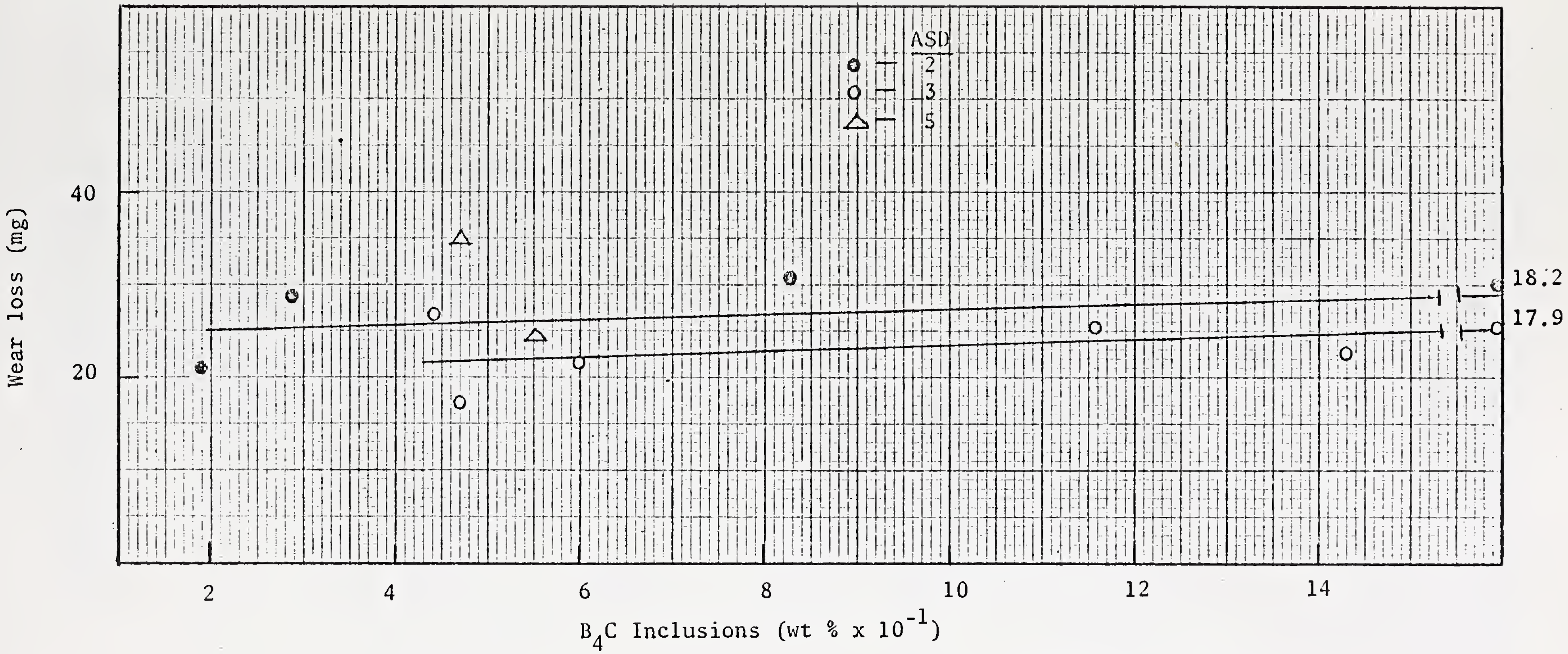
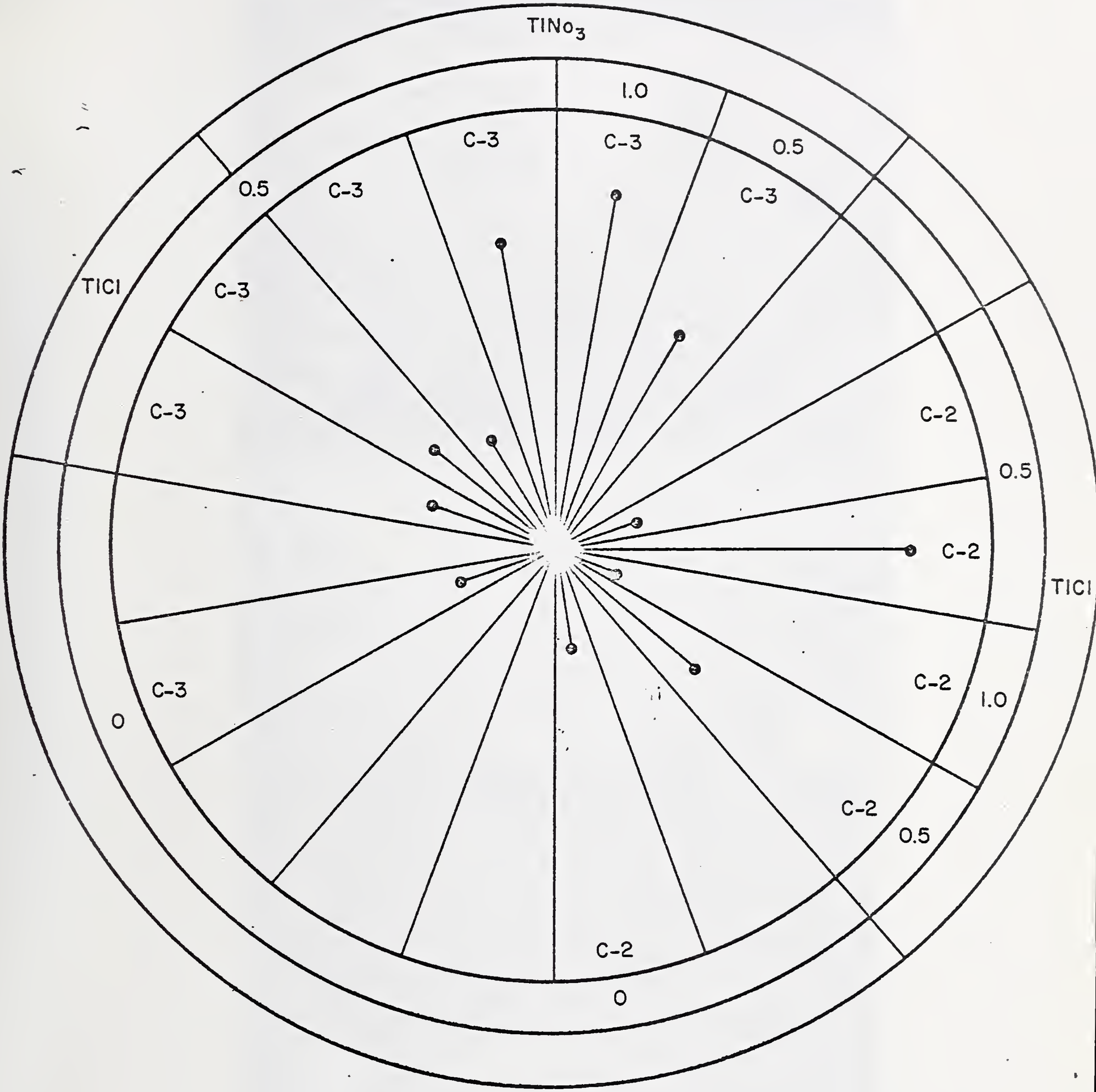


Figure 49. Inclusions in zinc versus wear-loss for deposits plated in a cyanide bath at 24°G using $TlNO_3$.



Temp. = 24°C B_4C - 30 g/1
C = Current density in asd
Inside ring = g/1 $TINO_3$ or TlCl
Radii = amt. inclusions .40 wt. %

Figure 50. Inclusions in zinc deposits using thallium.

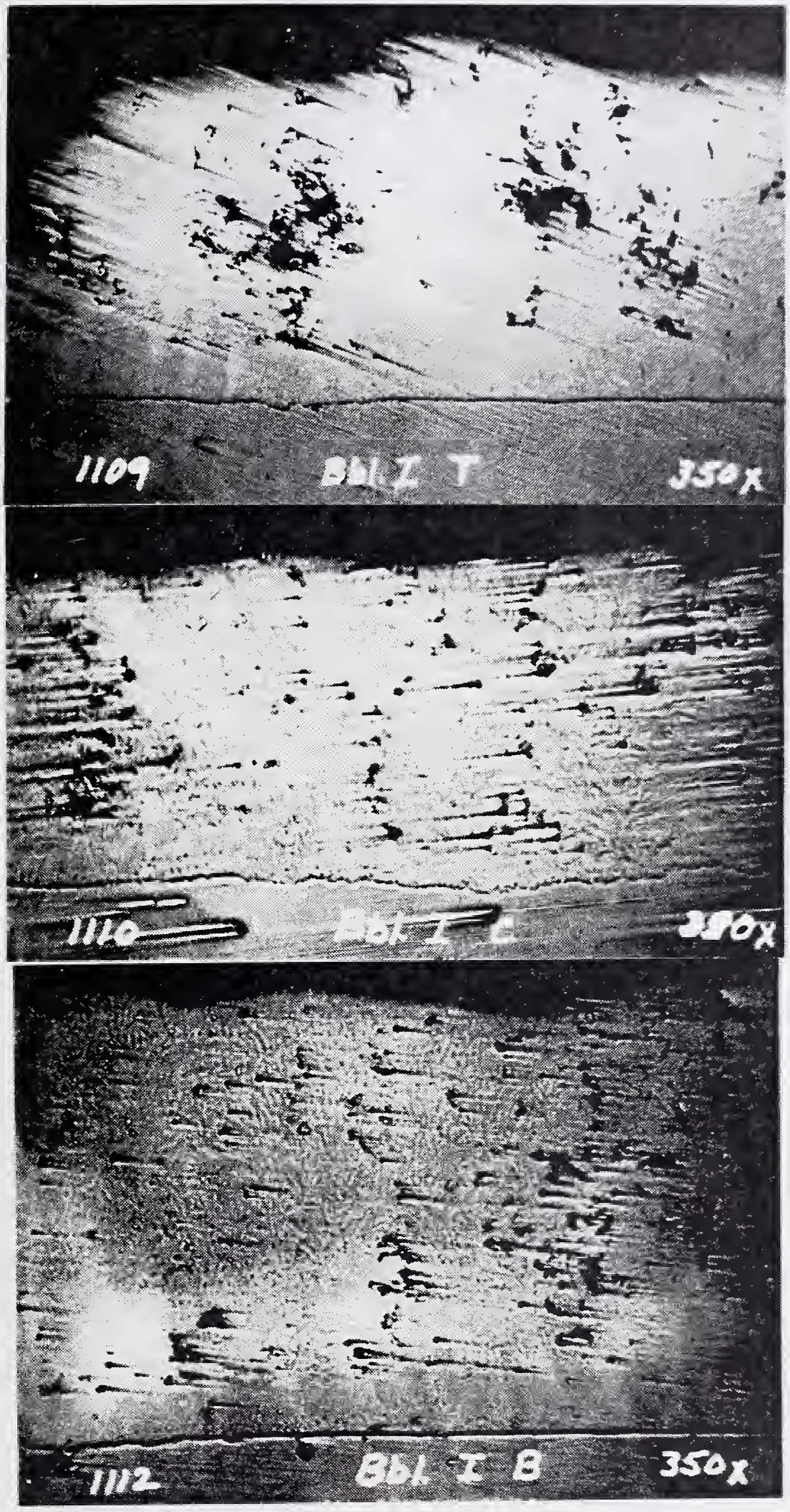


Figure 51. Chromium deposit on inside of stainless steel tube 3/8 inch ID x 20 inches long. Chromium deposited at 45°C/30 asd in tube in vertical position from bath containing 3 g/l Tl NO_3 and 30 g/l B_4C. Cross-sections taken from top, center, and bottom of tube. Hard particles resist polishing and leave "tails" of raised Cr. No etch.