AN ATTEMPT TO REFINE COPPER USING A CUPROUS ELECTROLYTE

BY
A. J. SCHUETTE
R. S. ZIEHN

ARMOUR INSTITUTE OF TECHNOLOGY

1913

A THESIS

PRESENTED BY

ADOLPH J. SCHUETTE and R.SEBASTIAN ZIEHN

TO THE

PRESIDENT and FACULTY

OF THE

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

HAVING COMPLETED THE PRESCRIBED COURSE

IN CHEMICAL ENGINEERING.

May 29, 1913.

APPROVED BY:

Harry McCormack

PROFESSOR OF CHEMICAL ENGINEERING

F. M. Rawson

DEAN OF ENGINEERING STUDIES

L. C. Monin

DEAN OF CULTURAL STUDIES

-TITLE OF THESIS-

AN ATTEMPT TO REFINE COPPER

THROUGH A

CUPROUS ELECTROLYTE

INTRODUCTION AND OBJECT OF THESIS.

When copper is refined electrolytically, the amount of it deposited upon the cathode is proportional to the current, the time, and the electrochemical equivalent of the metal. In the large refineries of today, the electrolyte used is a water solution of copper sulphate acidified with sulphuric acid, the latter a value as practicable, the resistance of the bath. In order to further decrease the resistance of the bath, the electrolyte is heated to about 70° C. With all economics included in the plant, the process has shown a current efficiency of a little over ninety-five per cent. This is for the multiple system. The series system is less efficient on account of short circuiting of some of the current through the sides and bottom of the tank, and through the slimes.

Theoretically, one ampere day, or twenty-four ampere hours should deposit practically 1 oz. of copper. This figure is arrived at as follows: 96500 ampere seconds or coulombs deposit 31.8 grams of copper from cupric electrolytes, provided no secondary reactions occur. Then one coulomb will give 31.8/96500 grams of copper. Twenty-four ampere hours, or 24x36000 coulombs will deposit

24x3600x31.8/96500 grams of copper or

24x3600x31.8x16/96500x453 = 1.005 oz. of copper.

Obviously, the only way to change the yield for the given quantity of current, is to change the electrochemical equivalent. This can be doubled by using a <u>cuprous</u> electrolyte.

It may be said at this point that the investigation was inspired by the Hoepfner Process, which was designed by Dr. Ludwig Hoepfner to serve as a commercial method of extracting copper and nickel from a complex copper nickel matte containing iron and other impurities, such as lead, arsenic and antimony.

This process, briefly, is as follows: The matte, finely ground, was extracted in wooden drums, first at ordinary temperatures, then at an elevated temperature produced by steam, with a solution of cupric chloride and calcium chloride, the latter being present to prevent hydrolysis of the CuCl formed. Copper and nickel from the matte go into solution, probably according to the reactions:

#1 $Cu_2S + 2CuCl_2 \quad 4\ CuCl + S$

#2 $Ni_2S + 4CuCl_2 \quad 4\ CuCl + 2NiCl_2 + S$

Ionically these reactions may be expressed

#1 $Cu^{++} + Cu \qquad 2Cu^{+}$

#2 $2Cu^{++} + Ni \qquad 2Cu^{+} + Ni^{++}$

The solution so obtained, when sufficiently reduced, was electrolyzed in a battery of cells of peculiar construction. Each cell was divided into an anode and a cathode compartment, the diaphragm being parchment paper covered with jute. The solution was pumped through the cathode compartments and anode compartments. That part of the solution which circulated through the cathode compartments has become practically copper free. This solution was next purified chemically with hydrogen sulphid, any remaining copper, the impurities lead arsenic and antimony being precipitated. The remaining impurity is iron. By adding bleaching powder to oxidize the bivalent iron to the trivalent state, and then lime,

the iron is precipitated in the form of ferric hydroxide. The solution now consists practically solely of calcium chloride and nickelous chloride. The solution was acidified with acetic acid and the nickel was precipitated in a two compartment cell, the diaphragm consisting of a nitrated cloth. The cathodes were moved. The solution now held only calcium chloride, and could be used to replenish the lixiviant in this constituent.

We shall now trace the course of the anode liquor and describe the changes it undergoes. While copper was deposited on the cathodes of the copper precipitating cells, chlorine was not liberated at the anodes, as it would appear. The chlorine combined (all but an insignificant amount) with the cuprous chloride of the anode electrolyte and changed this to cupric chloride. The solution, containing nickel cupric, cuprous, and calcium chloride as prin-

cipal constituents, along with the impurities, was trickled down a chlorine tower, where the reduced compounds were fully chlorinated. The solution from the tower was then united with the calcium chloride solution from the nickel electrolysis by which operation the regeneration of the original lixiviant was completed.

The anodes in this process were of carbon.

The process was a failure, owing to troubles with the diaphragms and the extracting vessels, beside imperfect extraction of the matte.

It was attempted to apply the cuprous bath to the copper refining. It will be understood, from a consideration of electrochemical principles, that a maximum saving of one-half the ampere hours used for a given quantity of copper refined through a cupric electrolyte, can be effected by using a cuprous electrolyte. This means a reduction in the mass cop-

per tied up in the conductors of the various circuits, or, if the same conductors were retained, a considerable increase in the capacity of the refinery would represent the advantage of using the cuprous electrolyte. A saving in power would also be had, for, while the drop across a cell would be greater than if a cupric electrolyte were used, as the Hoepfner process demonstrated, it would fall considerably short of being twice as great.

It was hoped to utilize a solution of ferric chloride and sodium chloride as electrolyte, the ferric chloride acting as follows:-

$$FeCl_3 + Cu \qquad FeCl_2 + CuCl$$

or

$$Fe + Cu \qquad Fe + Cu$$

the ferric chloride being regenerated at the anode:

$$Cucl \qquad Cu + Cl$$

$$FeCl_2 + Cl \qquad FeCl3$$

The sodium chloride was present to prevent the hydrolysis of the ferric chloride and of any

cuprous chloride formed.

At first, a solution was made up, containing

Ferric chloride - - - - - - 50 grams

Sodium Chloride - - - - - - 20 grams

Water - - - - - - - - - - - - 1 litre.

This solution gave unsatisfactory results in the cold, and similar results at about ninety degrees centigrade. The solution saturated itself with copper and the iron was precipitated, probably as basic chloride. A small quantity of glue was added to one bath and the electrolysis carried out hot. The deposited copper was much better than before. As this solution gave, results of such small promise, no data were taken on any run made with it. A deposit of copper, could however, be obtained, but it was very loose and irregular.

In hope of holding the iron in the solution, another solution of the following composition was made up:

Ferric chloride - - - - - 20 grams

Sodium chloride - - - - - (q.s. to saturate)?

Water - - - - - - - - - - - 1000 cc.

Several trials were made with this solution, at ordinary temperatures and at elevated temperatures and with a little gelatine in it. The results were all about the same. From this run on, two anodes were used, one on each side of the cathode, and each cathode was photographed. The iron precipitated as before, while the solution saturated itself with copper at the expense of the anodes. In this and the previous run the electrodes were put very close together and a current density of about four amperes was used, with the idea of keeping the electrolyte of fairly constant composition between the electrodes. This, however, did not seem to have any other effect than to decrease the resistance of the bath,

The next solution tried was a solution of ferric chloride alone in water. A twenty-five gram per litre solution was used. It gave no satisfactory re-

sults, the solution saturating itself in copper and loosing iron as a curdy brownish precipitate. The copper deposited was inadherent enough to become partly detached from the cathode on dipping into wash alcohol. Hence no data were taken on the runs made with this electrolyte. The current density was about two amperes.

The behaviour of a saturated solution of sodium chloride as electrolyte was next investigated. The cathode appeared to be covered with very finely divided cuprous oxide, which was showed very poor adhesive properties. This was carried out at a temperature of about twenty-four degrees centigrade.

Believing that the poor deposit of copper might be due to the fact that the copper was deposited from a chloride solution, it was decided to use a sulphate solution. As no ferric sulphate could be obtained, ferrous sulphate was substituted, and partly oxidized with hydrogen peroxide, and made strongly acid with sulphuric acid. This solution was experimented with, but gave cryst-

alline and non-coherent copper. A cathode was washed and photographed. It is shown in #2.

As the solution invariably saturated itself with copper at the expense of the anodes, it was decided to make up a solution and put into it a little cupric chloride. The solution was as follows:-

Ferric chloride -- - - - -	25 grams
(Na_2SO_4) - - - - - - - - - -	10 grams
Cupric Chloride - - - - -	5 grams
Water - - - - - - - - -- - - -	q.s. litre
Gelatine - - - - - -- - - -	small amount.

The sulphate was added with the idea that it might improve the deposit. The cathode of the solution is shown in #3.

The same solution was used for runs IV, V, VI, VII. It was made up in the following proportions:-

Ferrous sulphate - - - - -	20 grams
Sod. sulph. anhydr. - - -	20
HNO_3, sp. gr. 1.42 - -- -	6 cc.
H_2SO_4 sp. gr. 1.84 - - -	6 c.c.
Water - - - - - - - - - q.s.	1 .

The same solution was used for runs VIII & IX. was the same, except that most of the acid was neu ralized with sodium hydroxide solution.

Beginning with run #5, readings of current, voltage drop across the cell, and temperature of the bath were taken every ten minutes. The cathodes were weighed before and after the run. The electrolytes were analyzed after the run for copper. The anodes of runs #5, #6, and #7 were also weighed. It was from the cathodes of these runs that appreciable amounts of copper became detached. All of the cathodes were photographed shortly after removel from the bath, to record their appearance. It can be seen from an inspection of the prints that no cathode is absolutely free from nodular and crystalline protaberances, although some of the latter cathodes, where a rather low current density was used show a pretty fair surface.

To test whether any of the copper was actually transferred from anode to cathode in the univalent state, it is but necessary to calculate from the average values

of the data obtained, what the theoretical yield would be, using the cupric equivalent of copper, 31.79. If the actual yield was larger than the theoretical yield, very evidently some of the deposited copper must have come over in the cuprous condition, for which the equivalent is 63.57.

No. 5.

Time	Current	Electro Motive Force	Temperature	Resistance.
0	.850	.90	26.5°C.	1.059
10	.865	.80	26.5	.925
20	.875	.65	26.8	.74[illegible]
30	.875	.70	26.8	.800
40	.884	.70	27.1	.79[illegible]
50	.885	.68	27.5	.768
60	.885	.66	27.6	.745
70	.884	.68	27.8	.770
80	.885	.67	27.8	.757
90	.880	.67	28.0	.762
100	.879	.65	28.0	.739
110	.879	.65	28.0	.739
120	.879	.65	28.0	.739
130	.879	.65	28.0	.739
140	.877	.64	28.0	.740
150	.875	.67	28.0	.766
160	.878	.67	27.8	.76[illegible]
170	.874	.67	28.0	.762
180	.875	.69	27.8	.760
190	.872	.70	28.0	.803
200	.873	.67	28.0	.768
210	.871	.69	28.0	.791

Run 5 continued.

Time	Current	Electro Motive Force	Temperature	Resistance.
220	.873	.68	28.0°	.779
230	.873	.68	29.0	.779
240	.872	.69	28.0	.78
250	.871	.69	28.0	.79
260	.870	.68	28.0	.781
270	.871	.70	28.0	.804
Average	.871	.687	28.6°	

Run No. [illegible]

Time	Current	Electro Motive Force	Temperature	Resistance.
0	.851	.545	66°C.	.640
10	.858	.528	66	.616
20	.863	.500	66	.579
30	.865	.490	66	.567
40	.866	.484	66	.559
50	.865	.515	65	.595
60	.867	.510	65	.588
70	.869	.500	65.2	.575
80	.869	.495	65	.570
90	.870	.490	65	.563
100	.872	.460	65.2	.528
110	.873	.435	65	.498
120	.873	.406	65	.466
130	.873	.383	65	.439
140	.890	.295	67	.331
150	.890	.297	67	.334
160	.880	.299	67	.340
170	.885	.290	67.5	.328
180	.888	.270	68	.304
190	.890	.275	68	.309
200	.882	.280	68	.316

Run #6 continued.

Time	Current	Electro Motive Force	Temperature	Resistance.
210	.892	.280	67.8	.314
220	.892	.280	67	.314
230	.894	.275	66.5	.308
240	.895	.270	66.	.302
Average	.877	.394	66.2° C.	

Run #7.

Time	Current	Electro Motive Force	Temperature	Resistance.
0	.680	.837	86°C.	1.230
10	.700	.428	90.7	.611
20	.700	.400	85.5	.572
30	.717	.400	89.6	.558
40	.722	.398	90.0	.553
50	.726	.360	89.7	.496
60	.730	.370	89.5	.507
70	.733	.380	89.5	.518
80	.735	.364	88.5	.495
90	.750	.370	88.5	.493
100	.742	.342	90.5	.461
110	.750	.282	88.7	.376
120	.750	.285	88.4	.380
130	.750	.280	88.0	.374
Average	.737	.392	88.8°C.	

Run No.

Time	Current	Electro Motive Force	Temperature	Resistance
0	.855	.805	20°C	.942
10	.850	.748	20	.880
20	.849	..778	20	.918
30	.852	.742	21	.871
40	.864	.720	22	.834
50	.852	.722	22	.843
60	.850	.720	22	.846
70	.850	.720	23	.846
80	.850	.720	23	.846
90	.850	.720	23	.846
100	.850	.720	23.5	.846
110	.850	.720	23.5	.846
120	.850	.720	23.5	.846
130	.850	.700	24	.824
140	.850	.700	24	.824
150	.850	.720	24	.846
160	.850	.710	24	.835
170	.850	.700	24.5	.824
180	.850	.700	24.5	.824
190	.851	.685	24.5	.805
200	.857	.580	23.8	.677
210	.860	.640	23	.744
Average	.852	.6858	23.96	

Run #9.

Time	Current	Electro Motive Force	Temperature	Resistance
0	.862	.850	79°C	.987
10	.888	.55	79°C	.620
20	.879	.57	79	.649
30	.890	.55	90	.618
40	.890	.53	82	.595
50	.898	.51	80	.568
60	.899	.51	82	.567
70	.895	.49	82	.548
80	.905	.40	88	.443
90	.910	.40	87	.440
100	.910	.39	86	.429
110	.920	.35	88	.380
120	.920	.35	88	.380
130	.920	.32	88	.348
140	.920	.32	88	.348
150	.920	.34	87	.374
160	.920	.35	87	.381
170	.920	.35	87	.391
180	.920	.35	87	.381
190	.920	.32	81.5	.348
200	.930	.22	85.5	.237
210	.930	.25	85.	.269
Average	.9075	.421	84.8°C.	

Run #10.

Time	Current	Electro Motive Force	Temp.	Resistance.
0	.413	.41	80°C	.993
10	.413	.38	84	.919
20	.414	.34	90	.822
30	.415	.34	90	.819
40	.414	.34	90	.822
50	.418	.34	89	.813
60	.420	.35	85	.833
70	.420	.35	85	.833
80	.420	.35	90	.833
90	.422	.30	88	.712
100	.422	.30	88	.712
110	.422	.30	90	.712
120	.422	.25	90	.593
130	.422	.25	90	.593
140	.422	.25	86	.593
150	..422	.25	88	.593
160	.425	.25	89.5	.588
170	.425	.25	89.5	.588
Average	.4180	.311	84.°C.	

Run #11.

Time	Current	Electro Motive Force	Temperature	Resistance
0	.398	.785	21.3°C	1.97[illegible]
10	.400	.724	21.5	1.[illegible]
20	.400	.675	21.0	1.68[illegible]
30	.404	.600	21.0	1.486
40	.404	.605	21.0	1.497
50	.407	.575	22.0	1.413
60	.410	.550	22.0	1.341
70	.410	..550	22.0	1.341
80	.408	.550	22.0	1.3[illegible]
90	.410	.530	22.0	1.347
100	.410	.530	22.0	1.292
110	.408	.501	22.0	1.292
120	.408	.501	22.0	1.[illegible]6
130	.408	.501	22.0	1.[illegible]
140	.410	.500	23.0	1.[illegible]
150	.410	.501	23.0	1.[illegible]
160	.410	.500	23.0	1.[illegible]
170	.410	.500	23.0	1.[illegible]
Average	.407	.565	21.9°C	

Run #12.

Time	Current	Electro Motive Force	Temperature	Resistance.
0	.358	.71	77.0°	1.981
10	.358	.65	77.0	1.813
20	.358	.61	77.0	1.704
30	.360	.60	77.0	1.666
40	.361	.60	77.4	1.660
50	.361	.63	77.0	1.741
60	.362	.59	77.5	1.675
70	.364	.56	78.0	1.538
80	.365	.55	78.5	1.505
90	.365	.55	78.5	1.505
100	.365	.55	78.5	1.505
110	.365	.54	79.0	1.495
120	.365	.53	80.0	1. 49
130	.365	.53	80.0	1.440
140	.365	.53	80.0	1.449
150	.367	.51	80.0	1.390
160	.370	.50	80.0	1.357

Average .362 .573 79.5°C.

Run #13.

Time	Current	Electro Motive Force	Temperature	Watt hrs.
0	.341	.832	21°C	[illegible].140
10	.339	.835	21	[illegible].418
20	.342	.814	21	[illegible].379
30	.342	.779	21	[illegible].175
40	.342	.753	21	[illegible].080
50	.341	.723	21	[illegible].180
60	.342	.682	21	1.[illegible]
70	.342	.662	21	1.932
80	.346	.663	21	1.912
90	.342	.639	21	1.866
100	.341	..623	21	1.825
110	.342	.611	21	1.786
120	.344	.580	21	1.695
130	.344	.649	21	1.[illegible]2
140	.345	.640	21	1.915
150	.345	.651	21	1.937
160	.344	.660	21	1.920
170	.345	.670	21	1.9[illegible]
180	.345	.675	21	1.955

Run 116 continued.

Time	Current	Electro Motive Force	Temperature	Resistance
190	.345	.680	21°C.	1.971
200	.345	.690	21	1.[illegible]
210	.344	.695	21	2.020
220	.342	.700	21	2.013
Average	.343	.692	21°C	

Description of Apparatus and Arrangement.

The apparatus used in the work was as follows:-

Storage Battery.

Rheostats.

Ammeters.

Voltmeters.

Cells.

Copper Electrodes.

Electrode Holders.

Burners, stands, analytical apparatus, etc.

The rheostats, which were field rheostats, bore the following marks of identification:-

FIELD RHEOSTAT.

Cat. #43660	Form B1	D.L.	C.R.#174
Type F			Ohms, 250
Amperes 2.5 - 1.25			Volts, 500

General Electric Co.,

Schenectady, N.Y.

N.P. 3937-A 13

The Weston Ammeters bore the following numbers:-

51495

53126

These instruments are fairly accurate.

The Weston voltmeters bore the following numbers:-

#28108

Model 1, #16756

Glass cells, rather thickwalled, $2\frac{1}{2}$x4x$4\frac{1}{2}$" were used for cold solutions, while 500 c.c. beakers were used for the hot ones.

The electrodes, whose form is shown perfectly on the photographs, were cut from sheet copper, of a thickness of about one-sixteenth of an inch. They were numbered to keep account of them with certainty.

The electrode holders were of the spring type, accomodating a cathode and an anode on each side of the former. The electrode holders proper were fastened to a hard rubber plate, and to suitable binding posts.

Blast burners, ring stands, analytical apparatus etc. complete the list of apparatus.

The apparatus, as can be seen from the photograph, was set up in duplicate. In series, across the terminals of the source of current, were placed; the ammeter, the

rheostat, the cell. Across the cell was placed the voltmeter. The cell was set in a granite ware pail, and was prevented from touching the bottom of the same, by mea s of a piece of wire gauze bent appropriately. By this arrangement the electrolyte could be warmed very easily. The cells were filled with 300 c.c. of electrolyte.

Analysis.

The run being over, the electrolyte was made up to one litre in a volumetric flask, and transferred to an ordinary litre flask and labelled. The solutions were subsequently analyzed for copper, to get an idea of how much copper tho solution took from the anodes to saturate itself in this element for the conditions and concentrations obtaining.

The method used for the determination of the copper was as follows: Twenty-five cubic centimeters of the solution were measured into a beaker, treated with about one cubic centimeter of nitric acid, boiled, and made alkaline with ammonia. The nitric acid converted any ferrous iron to ferric. On making alkaline with ammonia, ferric hydroxide precipitated out. The solution was now boiled, and the ferric hydroxide filtered off, and washed several times with ammoniacal water. The filtrate contained the copper in the form of a deep blue cupri-ammonia compound. The solution

was made acid with acetic acid, potassium iodid solution was added, and the liberated iodine titrated with standard sodium thiosulphate.

The copper was calculated to grams per litre.

COPPER CONTENT OF SOLUTIONS.

Run	g.Cu. deposited	g.Cu./l.	Remarks
1			
2			Glue
3			Gelatine
4			"
5	1.061	2.30	"
6	3.103	2.95	"
7	1.120	2.25	"
8	Impure deposit	2.46	"
9	" "	1.14	"
10	.265	.73	Glue
11	1.235	1.04	"
12	.631	1.15	"
13	.226	1.52	"

Calculations.

Efficiencies On Basis Of Cupric Electrolyte.

Run	Cu obtained	T	Theoretical Cu	Efficiency
1				
2				
3				
4				
5	1.061	28.6° C	4.65	22.8%
6	3.103	66.2°	4.16	74.6%
7	1.120	88.8°	1.87	60.0%
8		24.0°	3.54	
9		84.8°	3.76	
10	.265	84.0°	1.41	18.8%
11	1.235	21.9°	1.37	90.0%
12	.631	79.5°	1.14	55.3%
13	.226	21.0°C	1.49	15.2%

DISCUSSION.

So far as our work has gone, we have demonstrated that neither ferric chloride nor ferric sulphate will react in the electrolytic cell so as to dissolve the copper from the anode in the cuprous state.

The iron, in the case of the ferric chloride is partially precipitated as a gelatinous mass, and partly on the cathode, causing the copper to be very loose and impure.

In the cases of runs #8 and #9 where the electrolyte was just neutralized with sodium hydroxide, curdy precipitates formed, and settled to the bottom of the cell and attached themselves to the cathodes, so that when it was attempted to wash the latter, the deposited copper also fell off and was lost.

The cathode of run #1, shown in the print, shows a crystalline, needle like surface. The solution was the chloride solution, used cold and without the addition of glue.

For #2, the same solution was used, a little glue being added, and the electrolyte being heated to about eighty-five centigrade. A rather high density was used, the average value being about four amperes. The deposit was quite thick, was matted rather loosely to the cathode, and possessed a decidedly nodular character.

Run #3 was carried out, using a sulphite solution, cold and with a slight addition of gelatine. The deposit seen in the picture rubbed off very easily.

The deposit obtained in run #4 was much better than any previous deposit, although it also showed the needle like crystalline structure, especially at the edges.

Run #5 gave a deposit, farily smooth, but slightly contaminated with iron at the dark part, shown by a yellow coloration.

The cathode of run #6 showed a good deposit, slightly crystalline at the edges. The deposit was quite adherent.

Run #7 gave a cathode, the deposit on which was smooth in the center and showed small nodules towards the edges and the top.

The deposit obtained in run #8 was contaminated with some iron as shown by a yellowish color acquired on long exposure to the air. The deposit rubbed off easily.

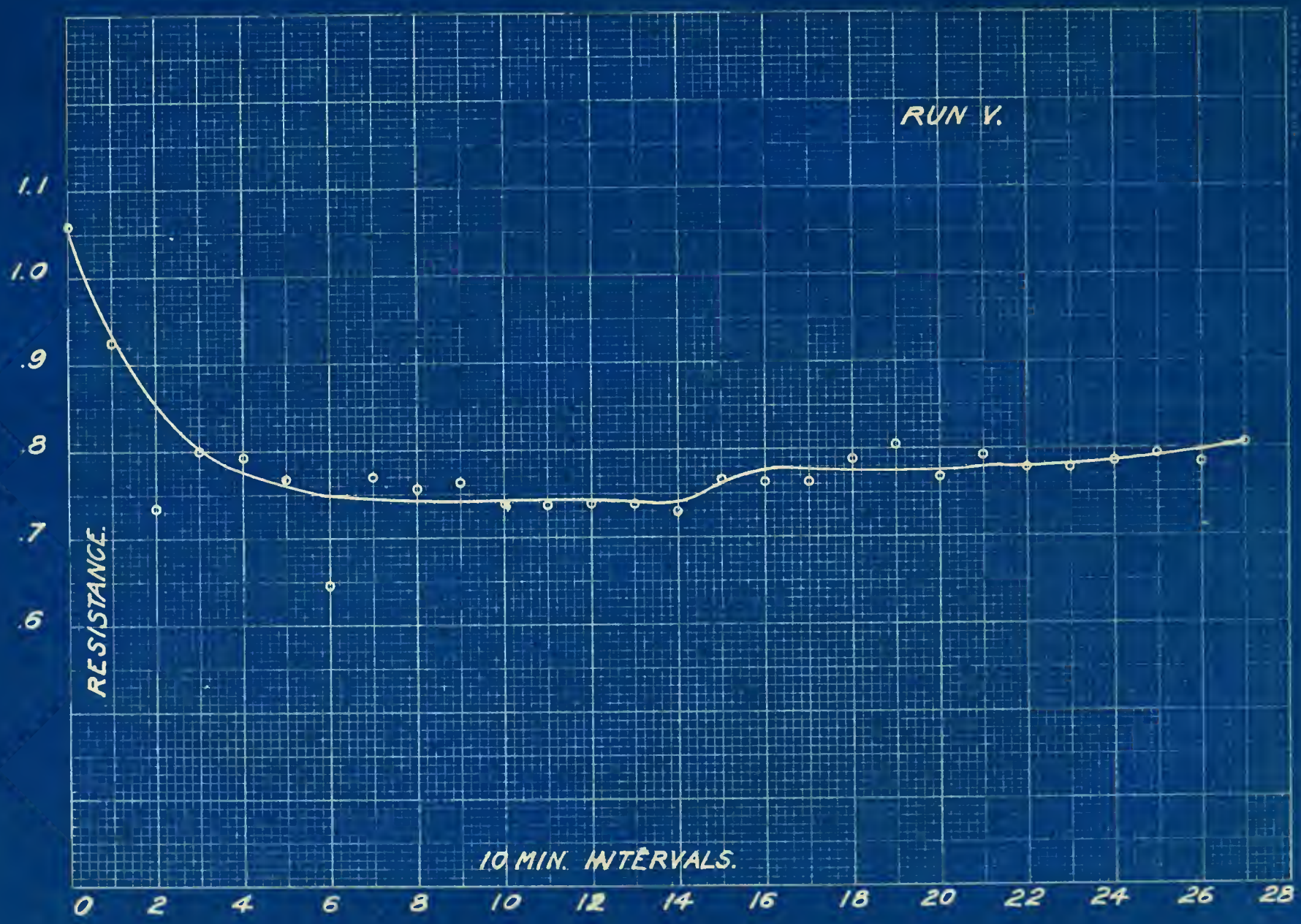
The deposit from run #9 was somewhat better, but also had particles of copper on its surface, which were very easily brushed off.

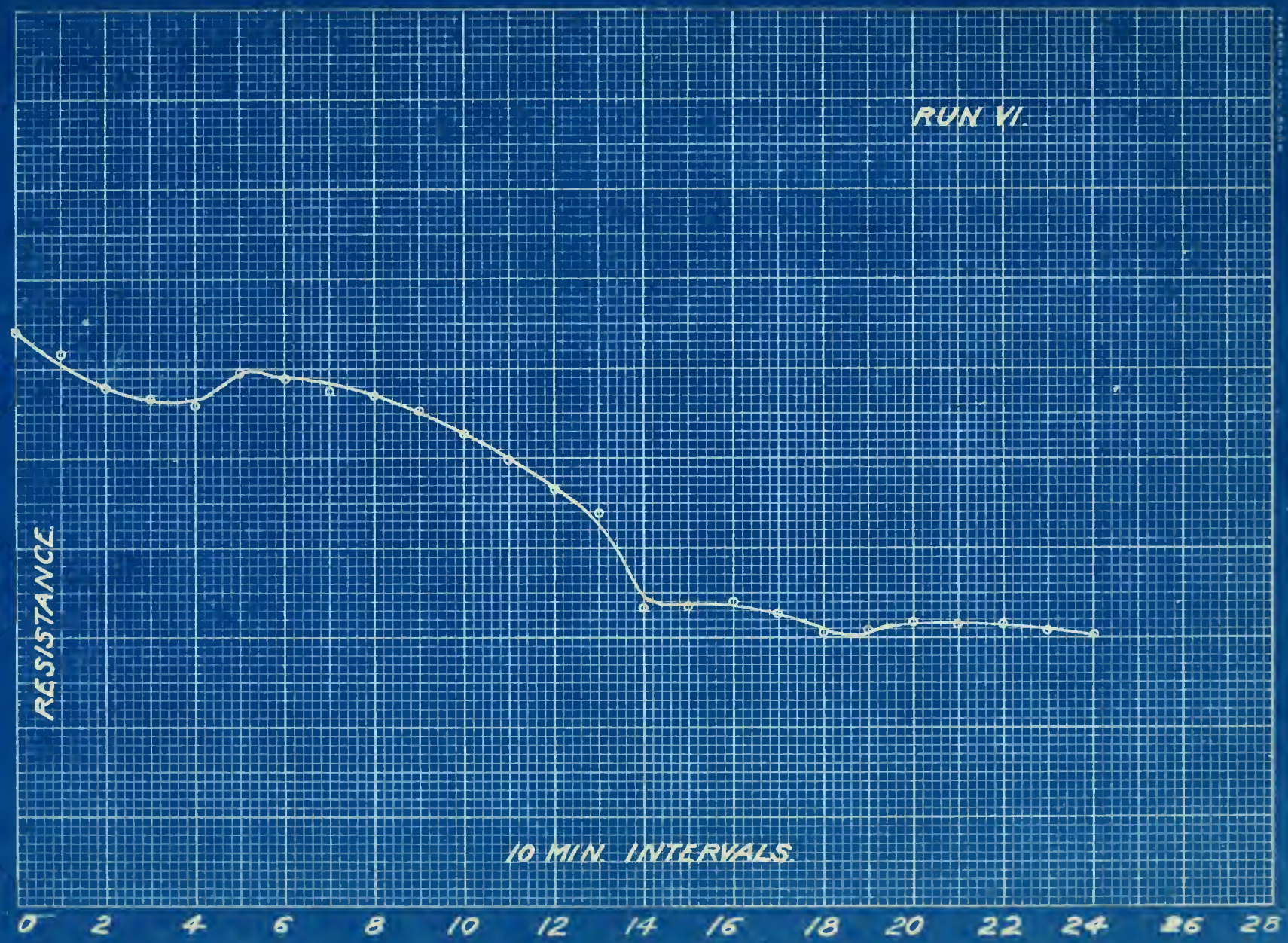
Cathodes #10 and #11 showed uniformly smooth deposits, that of #11 being slightly stained.

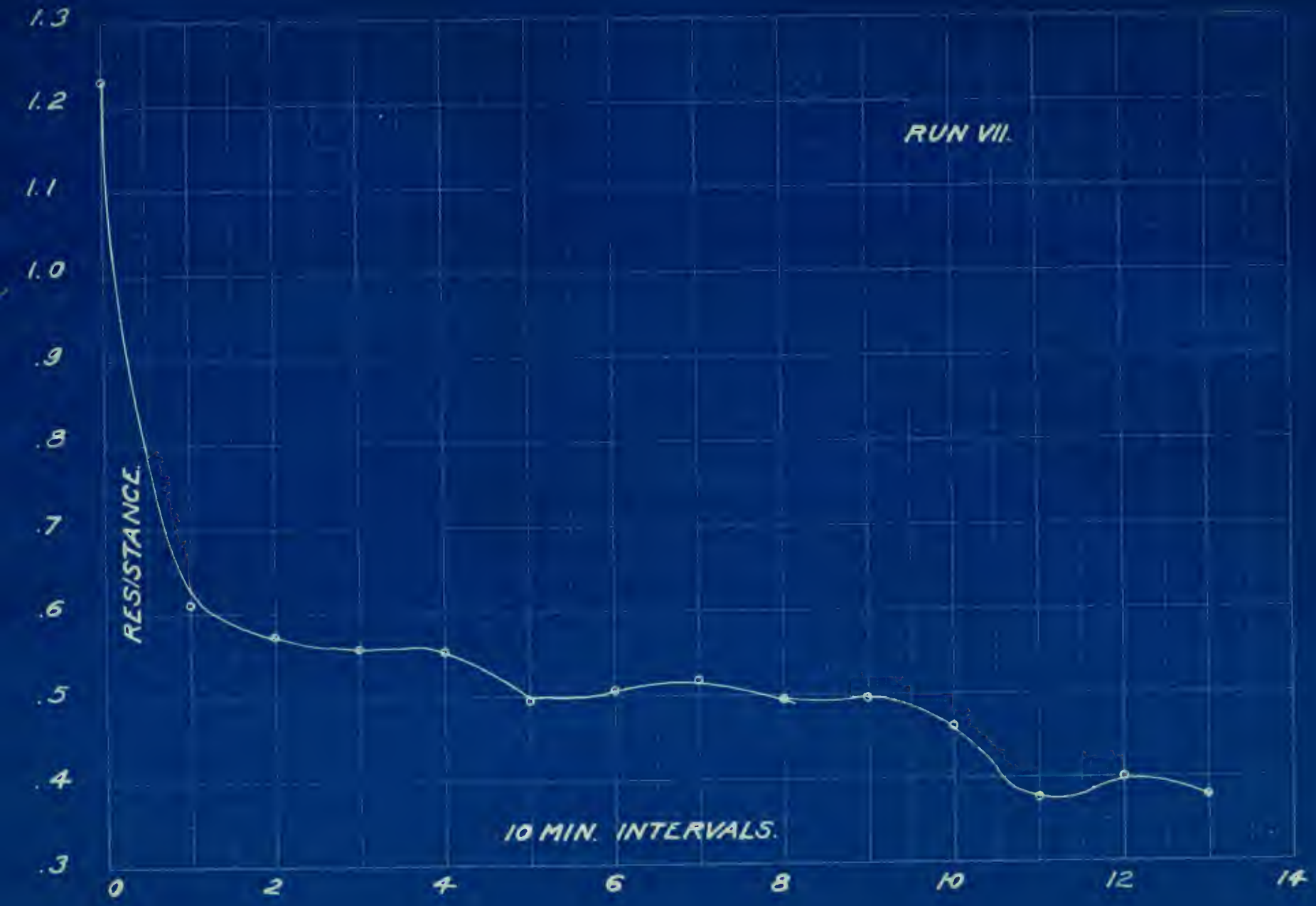
Cathodes #12 and #13 resembled #10 and #11 very much, #13 being slightly stained yellow at the sides.

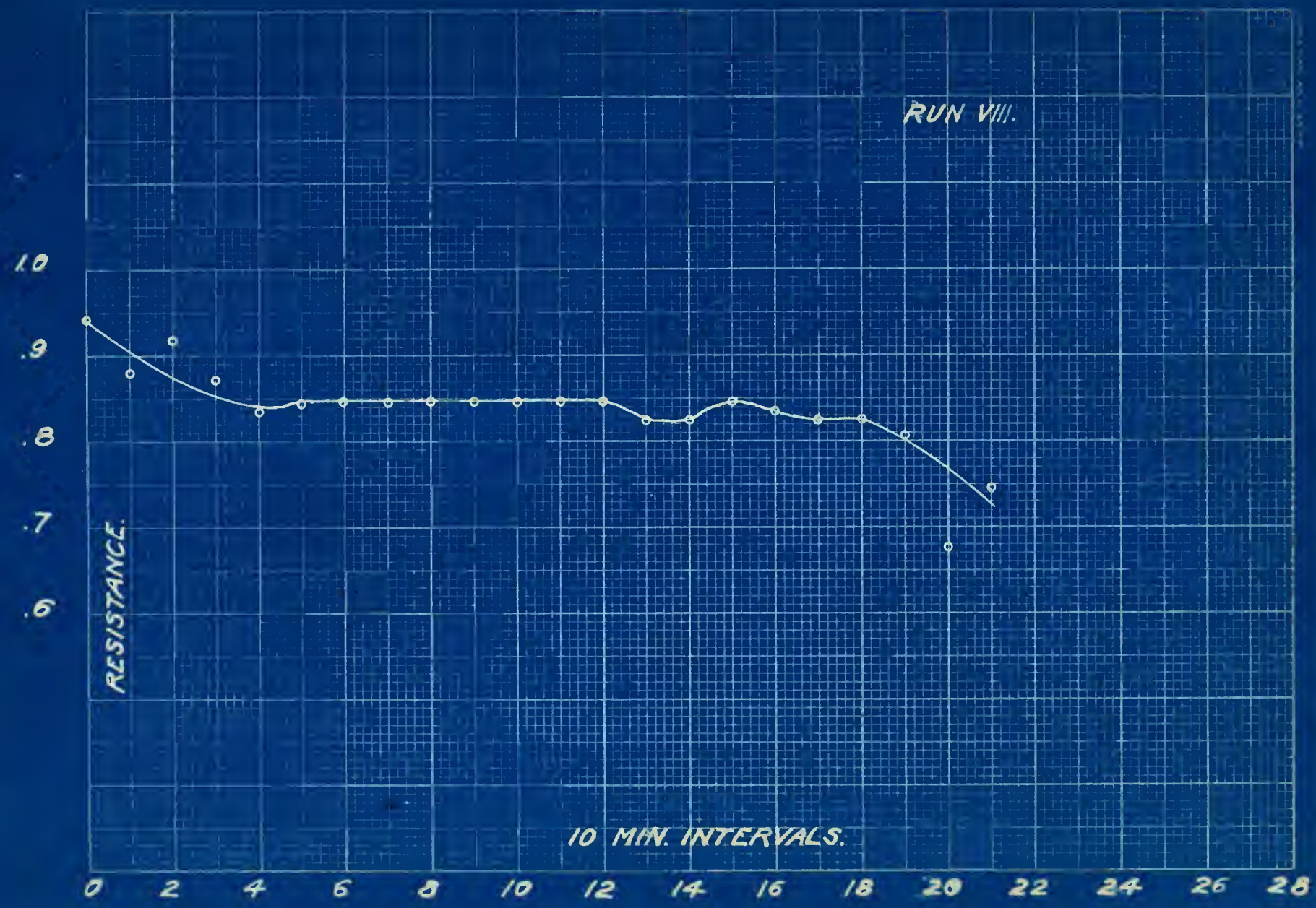
It had been intended to investigate next the behavior of a plain cuprous chloride solution and then an alkaline cuprous solution, if the time permitted, but, as this was not the case, the experimental work ended at this point.

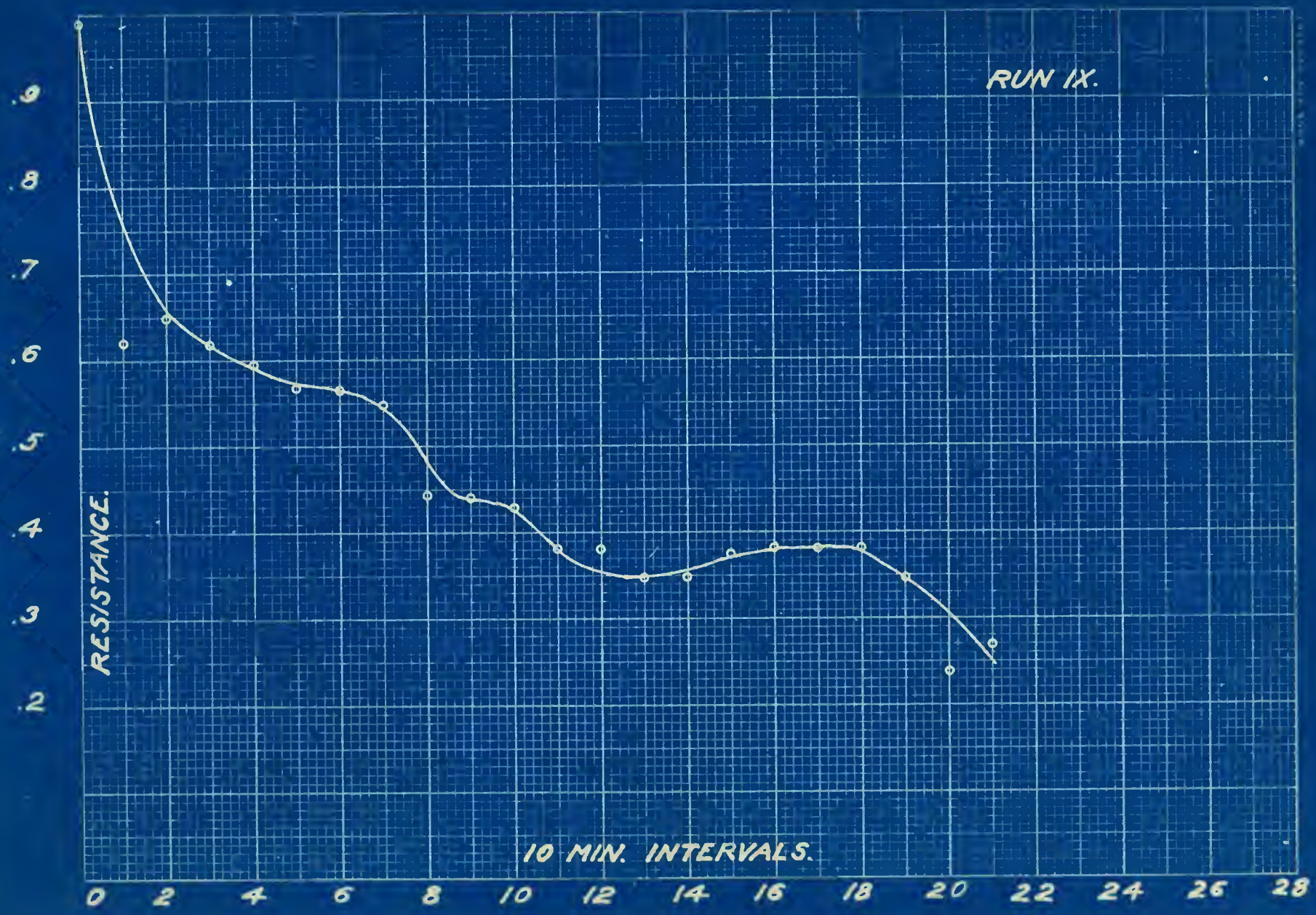
Curves were plotted for every run, showing the value of the resistance of the bath as the run continued.

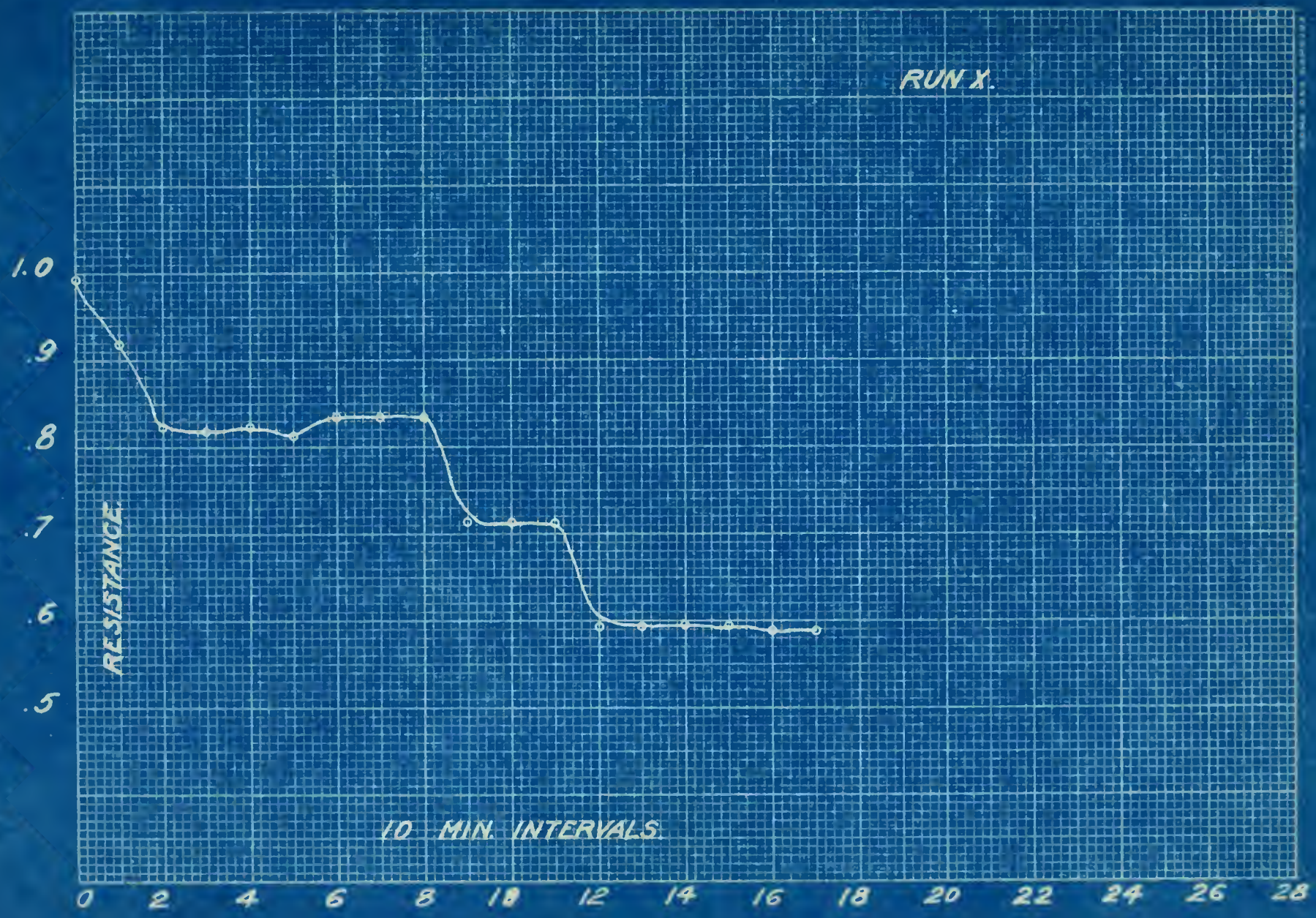

RUN V.
1.1
1.0
.9
.8
.7
.6
RESISTANCE.
10 MIN. INTERVALS.
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28

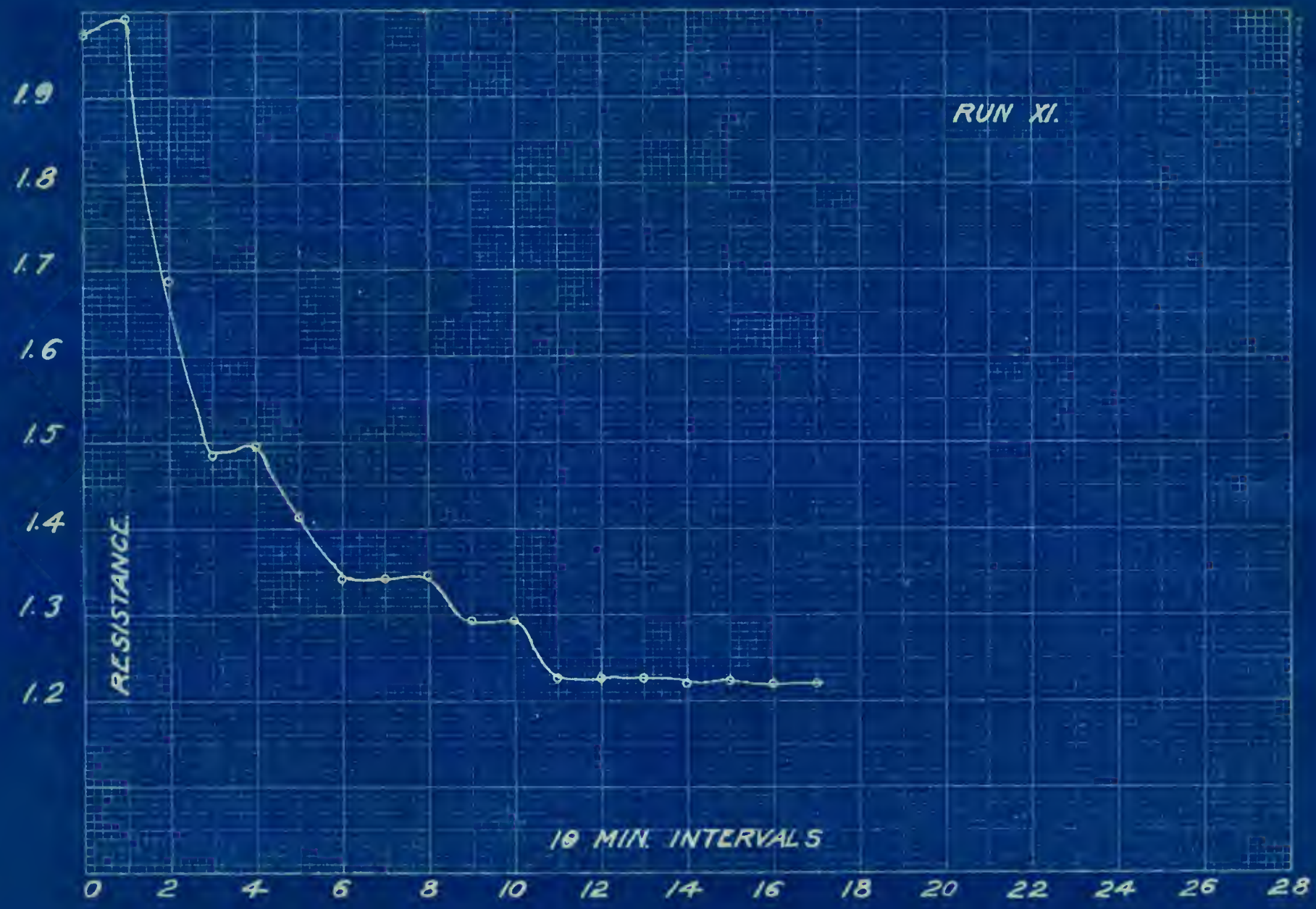

RUN VI.
.7
.6
.5
.4
.3
RESISTANCE.
10 MIN. INTERVALS.
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28

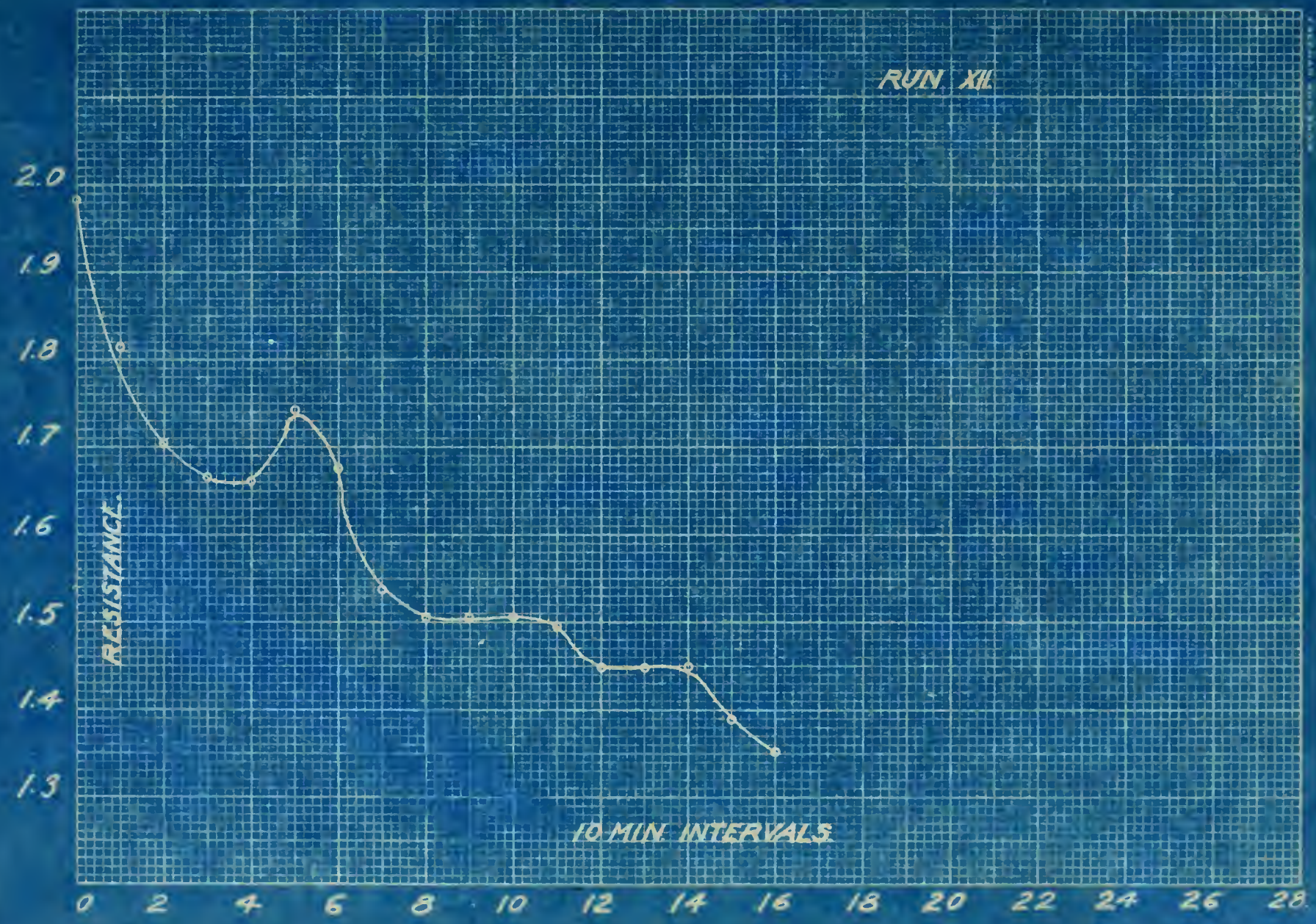

RUN VII.
RESISTANCE.
10 MIN. INTERVALS.
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
0
2
4
6
8
10
12
14

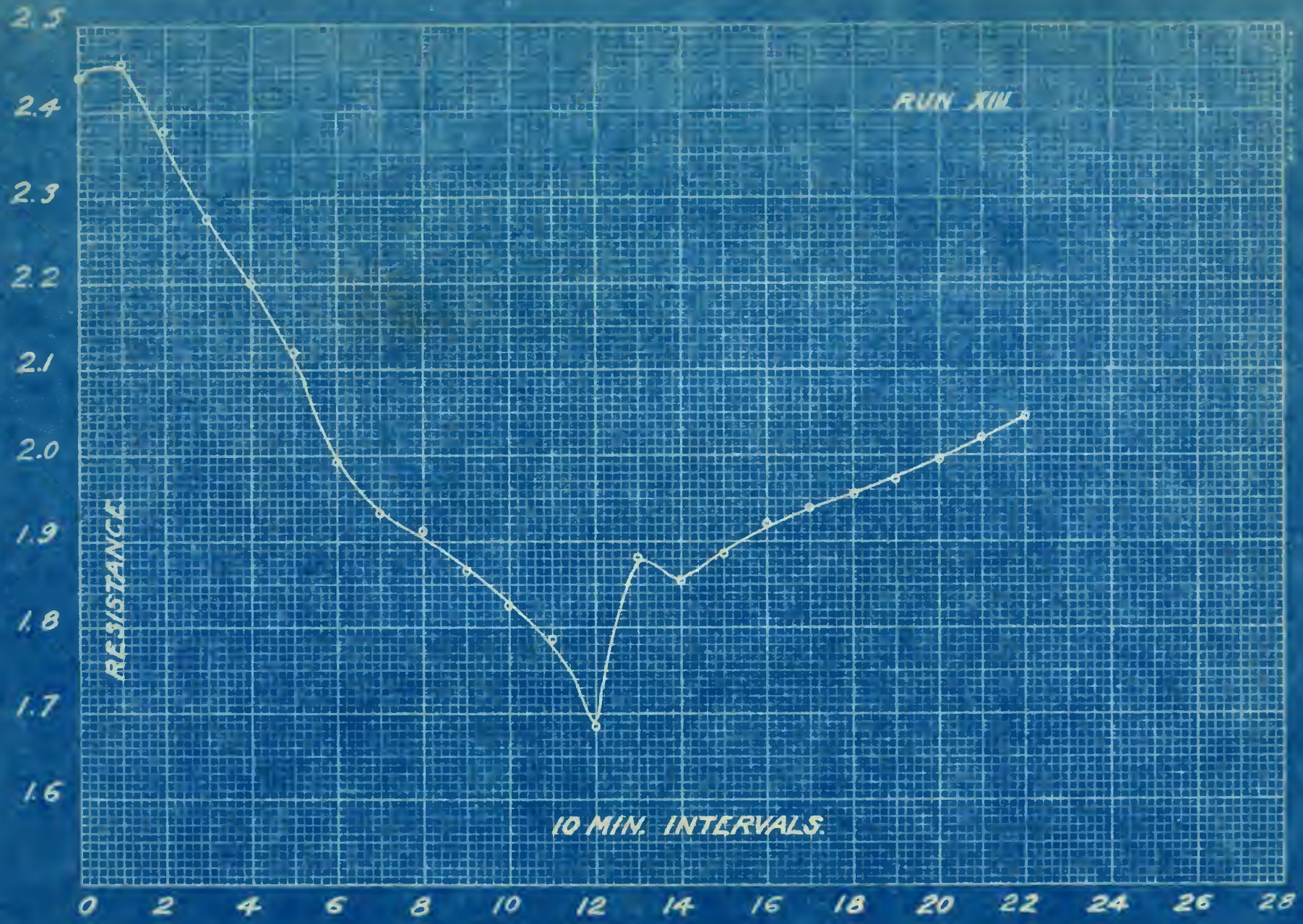

RUN VIII.
1.0
.9
.8
.7
.6
RESISTANCE.
10 MIN. INTERVALS.
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28


RUN IX.
RESISTANCE.
.9
.8
.7
.6
.5
.4
.3
.2
10 MIN. INTERVALS.
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28


RUN X.
1.0
.9
.8
.7
.6
.5
RESISTANCE
10 MIN. INTERVALS
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28


RUN XI.
RESISTANCE
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
18 MIN. INTERVALS
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28


RUN XII
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
RESISTANCE
10 MIN INTERVALS
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28


RUN XIII
RESISTANCE
10 MIN. INTERVALS.
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28