THE ELECTROLYTIC PREPARATION OF LEAD BASIC CARBONATE

THESIS FOR THE DEGREE OF M. S.

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Electrolysis

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THE ELECTROLYTIC PREPARATION
OF
LEAD BASIC CARBONATE

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I wish to take this means of expressing my appreciation to Dr. D. T. Ewing, whose supervision and counsel brought about the attainment of this thesis.

Basic lead carbonate has been known for many years as a preservative, having been recorded in the writings of Pliny as a covering for the hulls of ships. However, it was not used in their paintings, according to analyses made by Sir Humphrey Davy. The Greek author and scientist, Theophrastus, describes the preparation of white lead as follows: "Lead is placed in earthen vessels over sharp vinegar and after it has some thickness by a kind of rust, which it commonly does in about ten days, the vessels are opened, as it were, in a kind of foulness and the rust scraped off; the lead is then placed over the vinegar again, repeating over and over the same method of scraping it until the lead is wholly dissolved. The scrapings are then beaten to powder and boiled for a long time, and what at last subsides to the bottom of the vessel is cerusse."

This product was used extensively in Greece at that time as a cosmetic and as an eyesalve. Another method was in use in Rhodes, that of placing twigs in the jars and pouring over them acetic acid and then placing lead shavings on the twigs. The jars were then covered to prevent evaporation and after a period of time were opened and white lead found therein. These writers did not take into account the use of carbon dioxide in the air, as well as the moisture, in the formation of the desired compound. Rather they attributed the result entirely to the action of the acid.

These processes are closely approximated by two of the more modern methods, namely, the Dutch or stack process, and the chamber process. In the former, strips of lead are placed over pots containing acetic acid. There are several rows of these, piled one on another. The atmosphere is allowed to circulate throughout the system. The oxygen is necessary for oxidation and carbone dioxide also present in the air, forms the carbonate from the acetate. This process requires three months at normal temperature. The chamber process employs strips of lead hanging from bars in a large room into which carbon dioxide, air, water and acetic acid vapors are sprayed. This method comes to completion in about sixty days, during which time, a temperature of about 70° is maintained by hot gases and also by the heat of reaction.

Another important process is the French, which is done by treating basic lead acetate with carbon dioxide. However, this method is not overly popular or successful, due to the large amount of the normal lead carbonate which is formed.

There have been several electrolytic processes advanced, all of which consist, in the main, in the electrolysis of lead anodes or a lead solution, either in the cell or outside it. One of these, the Luckow process,may be used for making any insoluble salt. This employs both an anode and a cathode of lead. The important principle is that a very dilute solution of the salt will produce precipitation of the product, the salt referred to being sodium carbonate, which is present in a low concentration. There is present another salt, known as the secondary salt, which will, in reaction with the lead ion, form a soluble salt. Sodium acetate or chlorate may be used for this purpose. The object of the soluble product is to form the insoluble product away from the electrode, which would otherwise become coated with the basic lead carbonate, thus decreasing the efficiency greatly as the migration of the lead ion would be stopped almost completely.

The Sperry process, which is used by the Anaconda Lead Products Company in their factory at East Chicago, Indiana, was patented by E. A. Sperry (U.S.,1308948,1919). This is a continuous process as described hereinafter. The Principle is very similar to the Luckow process, in that it uses a salt which forms a soluble product at the anode; and the cathode solution, a carbonate, forms the basic lead carbonate, the formula for which is $2PbCO_3.Pb(OH)_2$. The more correct representation of the product may be shown better by this formula, $Pb(CO_3.PbOH)_2$.

The set up for production as given here is very similar to the actual plant, except that after the run in the plant a Doerr thickener is used to precipitate the solid. Before thickening, the liquid contains about 4% solids and is about 30% solids after thickening. It is then filtered, washed and dried to about .2% moisture in an oven. The filtrate, which is the catholyte or sodium acetate, is returned to the cell for further use. In the laboratory, no thickener was used, it being necessary either to filter the entire amount of catholyte or let it settle and decant the clear liquid. It was found, however, that slow bubbling of air through the liquid seemed to produce more rapid precipitation. It may be seen that this process is very inexpensive, inasmuch as the only raw materials needed are lead, water and carbon dioxide.

The experimental apparatus used consists of a large tank A, of about thirty four liters capacity, containing the anolyte, sodium acetate. There is a siphon arrangement from this tank to the cell B. This tube has four nozzles, which fit in the spaces between the anode and cathode. This supplies the solution in a steady flow through the cell. Tank A is kept full of anolyte at all times from a series of large carboys C, into which anolyte and the product are drawn from the bottom of tank B. The suspension is allowed to settle before the solution is used again. The catholyte is supplied in somewhat the same manner to the cathodes, which are enclosed in linen sacks. This is to keep the cathode sludge from dirtying the product. The catholyte is run into the sacks at the bottom, and the spent catholyte drawn off by a continuous siphon system D from the top of the sacks, and carried to the carbonating tower E, so that it may be used over. The lead anodes are about eighty-five square inches in area on one side. There are three of them so that there are four sides entering to the reaction. The total area is thus 2.38

square feet. There are two steel plates for anodes, which are about the same size. The carbonator is a glass tube packed with rocks so that the liquid will present a large surface to the gas, which is admitted at the side from a Kipp generator. The charged catholyte is then placed in Tank F for use in the cell again.

The anodes and cathodes are so made that they hang on the sides of the cell, and are connected to the switch board on opposite sides.

DATA

Series #I

Anode Plate Area - 2.38 square feet.

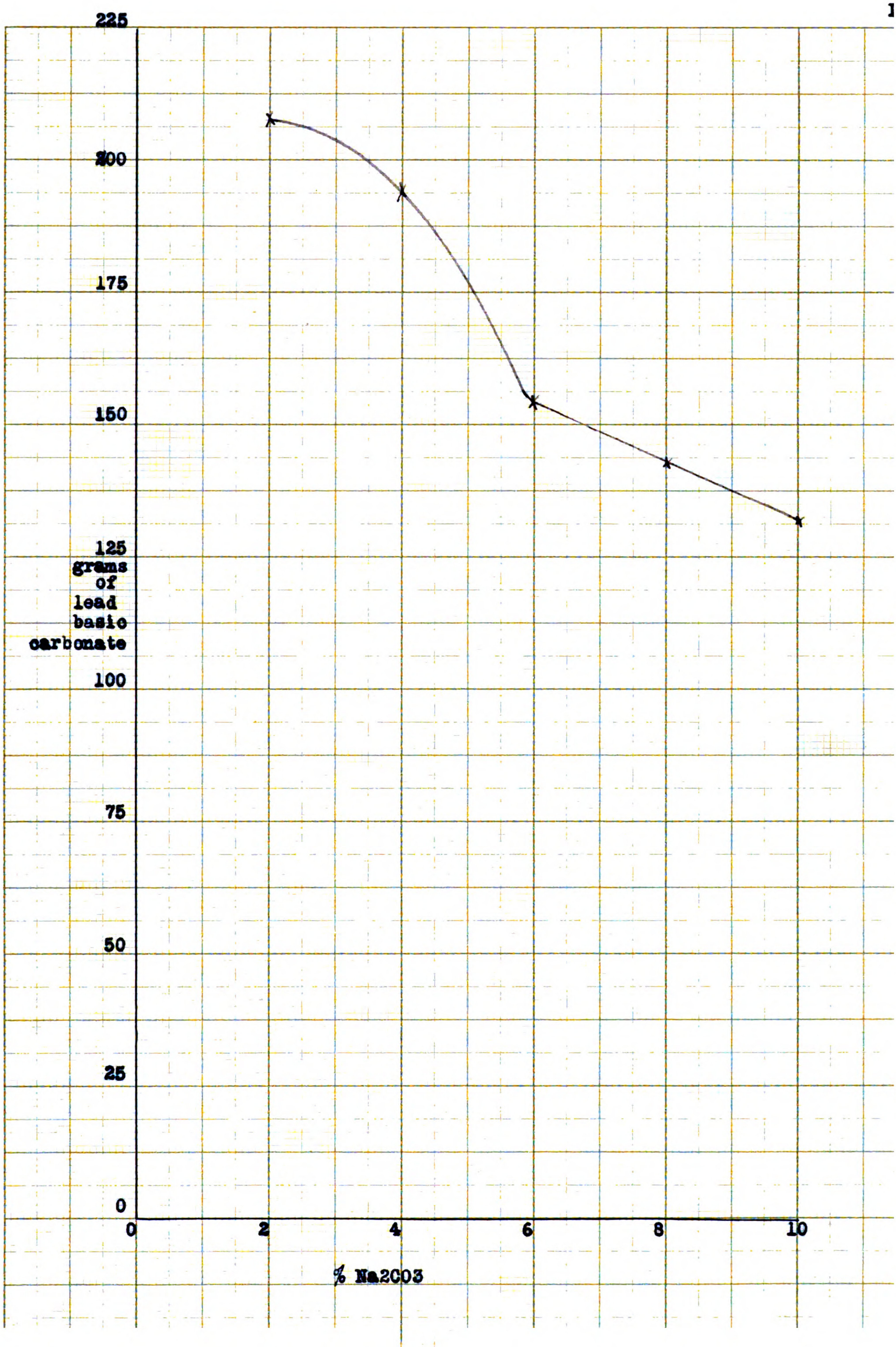
Temperature - 20° C

C.D. - 10 Amps.

Concentration Anolyte

Concentration Na_2CO_3	Yield	Analysis %CO_2	%Pb	Color
2%	207 Grams	14.03%	70.02	White
4%	192 "			Light green
6%	154 "			" "
8%	142 "			" "
10%	132 "			" "

These results seem to indicate other factors remaining constant, that with the increase in concentration of the catholyte, without an increase in the currect density seems to produce an inhibition in the amount of product formed and also a discoloration, as it may be seen that a smaller amount was formed at the higher concentrations of the catholyte and were colored green except the first product.


225
200
175
150
125
grams
of
lead
basic
carbonate
100
75
50
25
0
0
2
4
6
8
10
% Na2CO3

DATA

Series #II

Anode Plate Area - 2.38 Square feet.

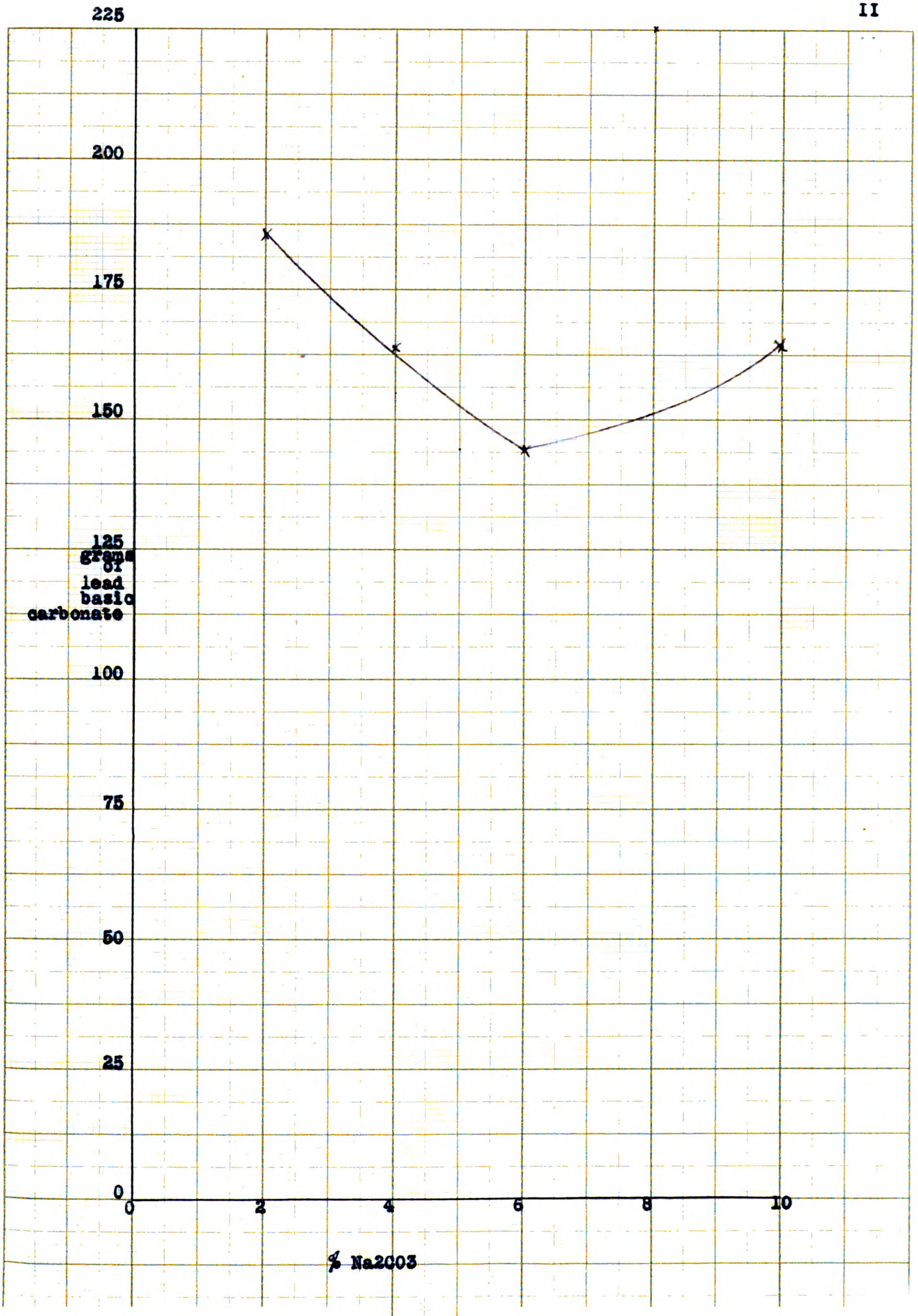
Temperature - 20° C.

Current Density - 13.5 Amps.

Concentration Anolyte - 2% $NaC_2H_3O_2$

Concentration Na_2CO_3	Yield	Analysis		Color
		% CO_2	% Pb	
2%	184 Grams	13.05%	71.3%	White
4%	164 "			Greenish White
6%	144 "			Green
8%	242 "			"
10%	164 "			"

These results show about the same as series #I, that an increase in the concentration of the Na_2CO_3 produces less rather than more white lead. Also, while the current density was increased, the yield decreased. The increase in yield at the end instead of decrease would seem to indicate the formation of some heavy product.


225
200
175
150
125
100
75
50
25
0
grams of lead basic carbonate
0
2
4
6
8
10
% Na2CO3

DATA

Series #III

Anode Plate Area - 2.38 Square Feet.

Temperature - 20° C.

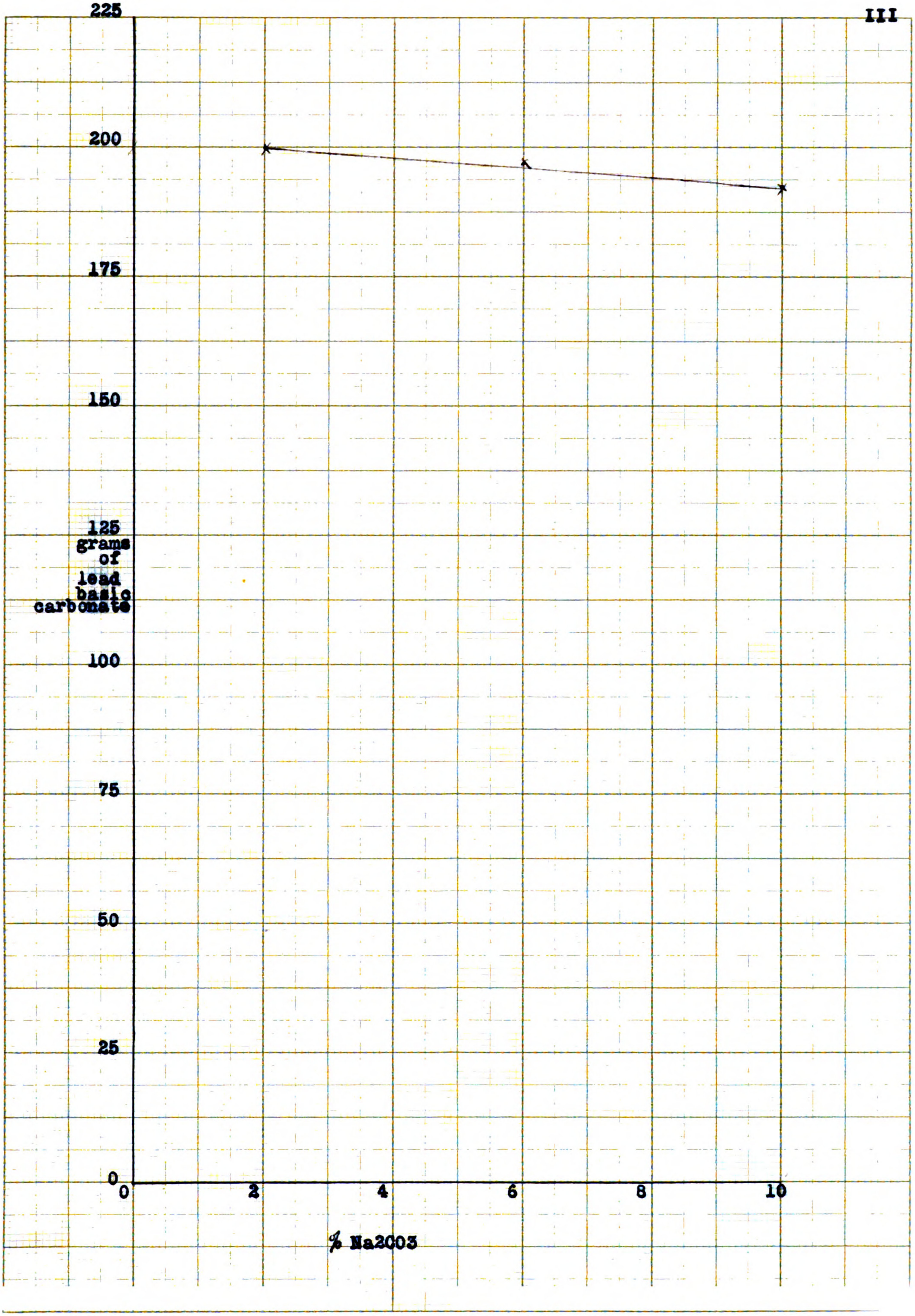
Current Density - 16.8 Amperes

Concentration Anolyte - 3% $NaC_2H_3O_2$

Concentration Na_2CO_3	Yield	Analysis % CO_2	% Pb	Color
2%	200 Grams	13.92%	74.6%	White
6%	196 "			Brown Yellow
10%	190 "			Light Brown

There is another effect noticed here, that of the formation of lead Peroxide at the anode. Some of it was retained but some was carried over with the product. Here, also, the current density was increased again, but the yield was still lower than the first run.

After this, I decided to regulate the flow. It took about ten runs before I was satisfied. After regulating, the anolyte flowed at a rate of a liter every half minute, andthe catholyte of a liter every minute and a half.


225
200
175
150
125
grams of lead basic carbonate
100
75
50
25
0
0
2
4
6
8
10
% Na2CO3

DATA

Series #IV

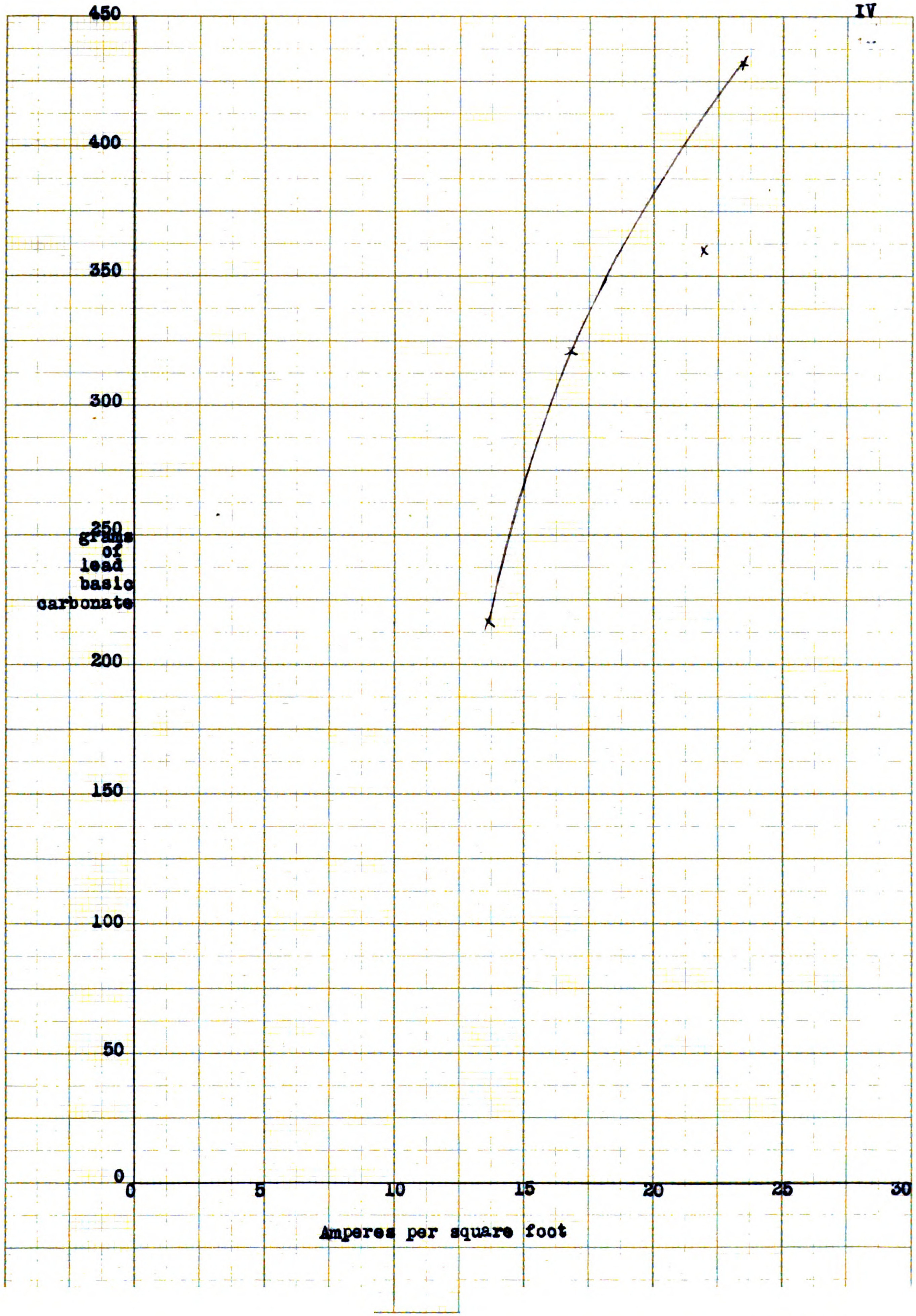
Anode Plate Area - 2.38 Square Feet.

Temperature - 20° C.

Concentration Anolyte - 1% $NaC_2H_3O_2$
Catholyte - 2-4% Na_2CO_3

		Analysis		
C.D.	Yield	% CO_2	% Pb	Color
13.5	216 Grams	12.04%	76.3%	White
16.8	320 "	10.06%	78.16%	"
21.9	360 "	9.8 %	85.2 %	"
23.5	432 "	10.9 %	79.34%	"

It was at this point after I got the flow regulated, and the carbonator adjusted that the runs were all a good clear white. Run #3^{4} above comes closest to the standard as given by the Anaconda Lead Products Co., about 11.15% CO_2 in the sample.


450
400
350
300
250
200
150
100
50
0
grams of lead basic carbonate
0
5
10
15
20
25
30
Amperes per square foot

DATA

Series #V

Anode Plate Area - 2.38 Square Feet.

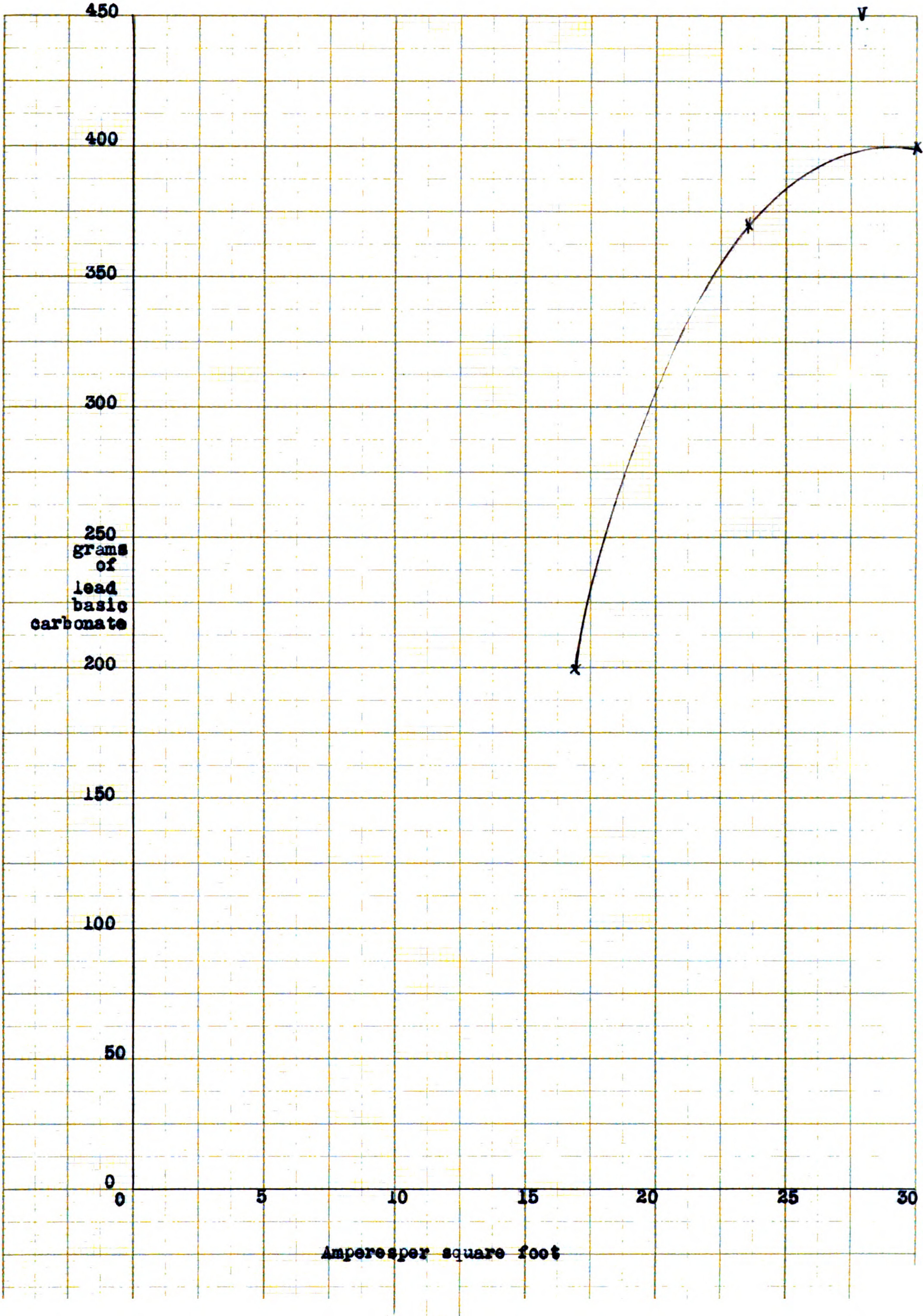
Temperature 20° C.

Concentration Anolyte - 2 %$NaC_2H_3O_2$

Catholyte - 2-4%Na_2CO_3

		Analysis		
C.D.	Yield	% CO_2	% Pb	Color
16.8	200 Grams	10.16%	79.33%	White
23.5	370 "	10.42%	78.62%	"
30.2	400 "	11.34%	81.01%	"

This series did not differ much from the preceding one, except that a higher current density was reached, an amperage that could not be obtained except by the higher concentration of sodium acetate. Some lead metal was formed at the cathode in this run.


V
450
400
350
300
250
grams
of
lead
basic
carbonate
200
150
100
50
0
0
5
10
15
20
25
30
Amperesper square foot

DATA

Series #VI

Anode Plate Area - 2.38 Square Feet

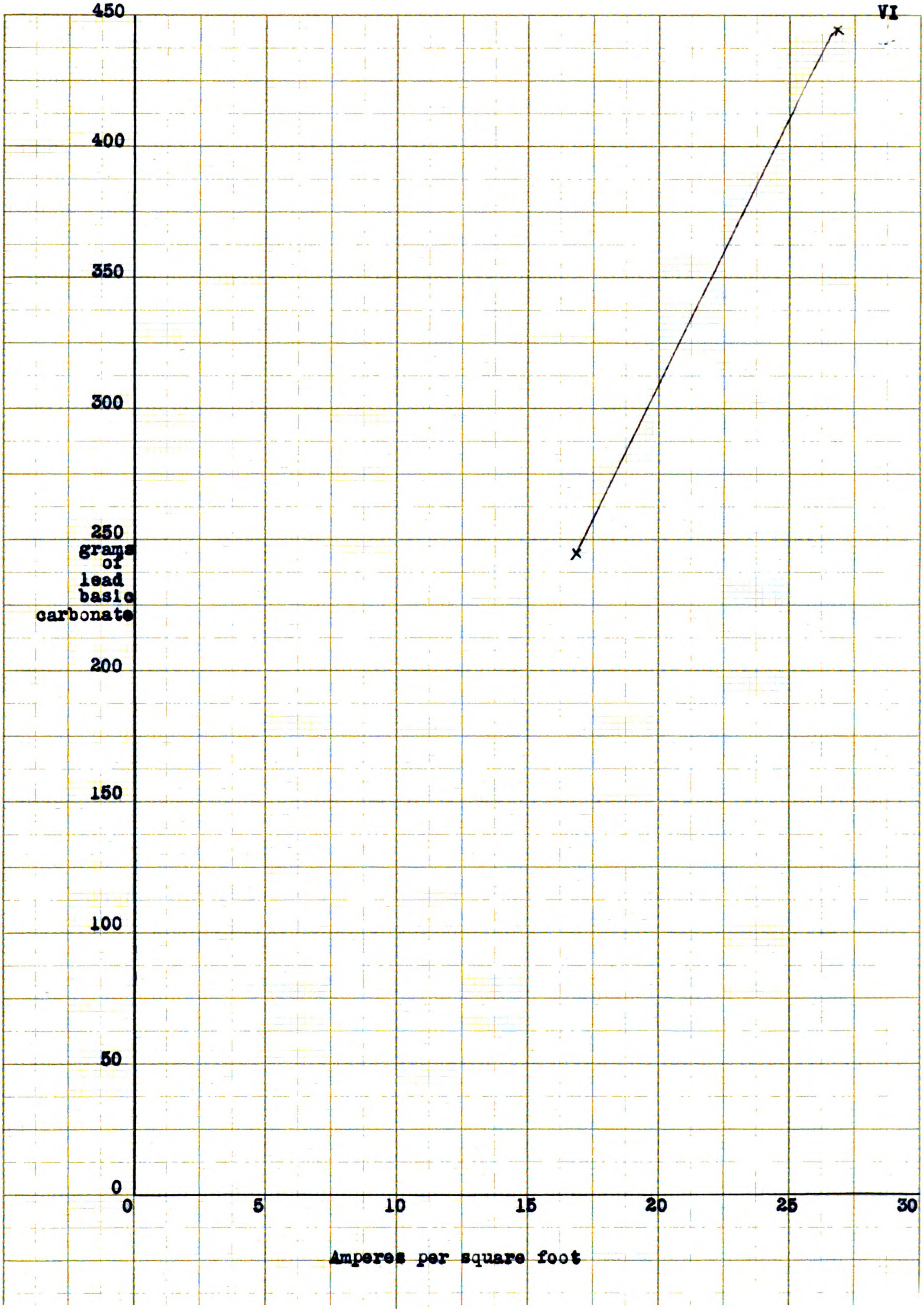
Temperature - 20° C.

Concentration Anolyte - 2 % $NaC_2H_3O_2$

Catholyte - 2-4% Na_2CO_3

C.D.	Yield	Analysis % CO_2	Analysis % Pb	Color
16.8	275 Grams	10.9 %	80.9%	White
26.8	445 "	11.26%	79.9%	"

These two runs were made over a longer period of time to show that production could be carried out over a long period of time in the laboratory. As may be seen from the analysis, the results were good.


VI
450
400
350
300
250
grams of lead basic carbonate
200
150
100
50
0
0
5
10
15
20
25
30
Amperes per square foot

This experiment was first set up on a small scale to determine if it could be worked in the laboratory. The set up was, on the whole, the same as the one described here, except that the lead plates were about half the size of the ones used in the regular outfit. About ten runs were made with this outfit and some products were obtained. These were discarded without analysing. Some difficulty was experienced, one of which was due to the fact that reservoir tanks were too small. Neither was there any provision made for the settling out of the product, which was quite finely divided and prone to stay in solution for some period of time. After it was seen that the process could be made to work, a large plant was made which has been described before. The Anaconda people use diaphragms of Irish linen around the cathodes, but since the sole purpose of the diaphragm is to keep anode sludge, spongy lead and iron rust from polluting the product, linen of the same texture as sheeting was used. The size of the particle that could pass through the cloth was not an important factor.

This plant was designed to draw a large amperage, so that it was necessary to construct a switchboard. Cast iron grids were used as resistors, and hooked up so that the amperage could be varied. Copper cable, size #0, was used for the connections. As there was no ammeter available for the amperages as high as was necessary for the cell as designed, a shunt, having a voltage drop of fifty millivolts for two hundred amperes, was hooked inthe line. The shunt was connected to a millivoltmeter and the drop in millivolts read. The millivolt meter read up to 100 by two's, so that it was necessary to multiply each scale division by eight to determine the amperage. This was first calibrated by balancing it with another ammeter on the lower ranges.

At first, a series of runs was made with the concentration of the anolyte constant, while the catholyte concentration was varied. The first product was white and the remainder was green. The second series had a higher concentration of anolyte, while the catholyte was changed as before. The results were about the same as the first series. The third series gave still another increase to the anolyte concentration, with the results staying about the same. The conclusion could be drawn that the best results came from the lower concentrations of the catholyte. It was also noticed that with the higher concentrations of the latter that there seemed to be a loading effect. In other words, the anolyte would take up carbon dioxide until the production of white lead was inhibited entirely. The green color was also produced at the higher concentrations, which was due to some factor which I was unable to determine. Another difficulty was the production of lead peroxide at the higher concentrations of the catholyte. This would seem to follow, as lead peroxide at the higher concentrations of the catholyte, is made normally in a strong solution of sodium carbonate. This would deposit directly on the lead and prevent the lead ions from leaving the electrode. After a short length of time the anode would be completely covered. Then, too, if only a small amount was formed, it was very likely to drop off and would color the lead carbonate brown. This happened in the 6% sodium carbonate, 3% sodium acetate run. Another run which was not listed gave the same results. These results also made it clear that the flow was a factor which could not be overlooked. There were about ten runs made in which the flow was experimented with, for which the product was not retained. The analyses determined the most satisfactory flow to be two liters per minute for the anolyte and .66 liters per minute for the catholyte.

After the concentrations of the two solutions had been investigated and the flow regulated, runs were made to determine the most satisfactory current density. As the cell was first set up, it was planned to have four anodes and three cathodes. It was found that these were so close together that the cloth diaphragms, distended with the load of solution, would touch the lead. While this did not cause a short, it had a serious tendency to decrease the efficiency of the cell, so that it was necessary to remove one of each at this point. The linen was then more firmly restrained by a rubber binding. All the parts were of rubber or glass, as the causticity of the basic solutions was, while quite dilute, nevertheless strong enough over a period of time to have a very strong corrosive action on wood, metal, stone or paint.

By changing the current density, the amount of the product and the character can be radically changed. Also, if the current density is too high, there is a large amount of spongy lead formed which accumulates at the cathode on both the inside and the outside of the cloth sack, which will cause some impurities to be present if it is not removed. This may be easily done by passing the anolyte and the suspended product through a coarse cloth directly on its leaving the cell. This serves very well to strain out the large particles of lead while the product passes through with ease.

There is one factor in the process as outlined here, which tends for further economy, namely, that the impurities in the metallic lead, while they may form products of some sort, are retained on the anode and may be washed off at the end of the run. This obviates the purifying of the lead. Spongy lead was formed on some of the longer runs at high current densities, which would seem to indicate that the flow of catholyte was insufficient to precipitate the lead ions, thus giving them an opportunity to get to the cathode and be reduced again to lead. This could be corrected by lowering the current density or increasing the flow. The former was the better solution to the problem.

Some of the product was ground in a mortar to a very fine powder, which was then mixed with linseed oil, to form white lead in oil. Some was also mixed into paint, and as raw oil was used, and it was a very slow drying job.

A sample of electrolytic lead chromate was also ground and mixed into pigment. Some of the pigment was then mixed half and half with white lead and diluted with oil and turpentine to a proper consistency. As paints, both had good covering and hiding qualities.

The samples were analysed in the following manner. An aspirator is charged with sulphuric acid and weighed. The sample of white lead is added and weighed again. This gives the weight of the sample. The sulphuric acid is then let down on the sample through a funnel. After the reaction has come to an end and the carbon dioxide has all bubbled through the small drying chamber, air is drawn through the bottle to rinse it out and clear out all the carbon dioxide. The apparatus is weighed again. The loss in weight is the carbon dioxide. The lead sulphate is insoluble and is digested, filtered, dried and weighed to determine the amount of lead in the sample. The standard amounts are given by the Anaconda Company as 11.35% $CO2$ and 80.14% Pb.

In conclusion, it is noted that the best yields of basic white lead are obtained under the following conditions, namely, 2% solution of sodium acetate, a 2--4% solution of sodium carbonate, and the current density 16.8 amperes per square foot. The flow of anolyte is two liters per minute and .66 liters per minute for the catholyte.

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