ELECTROLYTIC PREPARATION OF LEAD CHROMATE

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—

TABLE OF CONTENTS

ELECTROLYTIC PREPARATION OF LEAD CHROMATE

INTRODUCTION

Most of the work in this investigation was devoted to a study of the various factors which effect the electrolytic preparation of lead chromate. These factors include current density, composition of electrolyte, temperature and cell design.

The first electrolytic process for the electrolytic preparation of insoluble compounds was developed by Luckow. For such preparations he recommended a solution of 1.5% of a mixture of 9 parts of $NaClO_3$ and 1 part of $Na\ CrO_4$. This was electrolysed between a pure lead anode and a hard lead cathode. The anodic current density was about .24 amp/dm^2 and bath voltage being 1.4 volts.

These processes were later studied by LeBlanc and Bindschedler, Miller, and Gillett. They worked with different secondary salts at different concentrations and mixtures. The effect of temperature was also studied.

It would be expected that the precipitated particles by the electrolytic process would be finer the higher the concentration and the greater the current density. However, the above investigators found that if very low concentrations of the precipitating salt and low current densities were not used, adherent deposits on the anode would be formed instead of fine precipitates.

In the attempt to prepare electrolytic lead chromate the cell would yield $PbCrO_4$ for a short time and then a mixture of $PbCrO_4$ and PbO would form. This would give an undesirable color. The two opposing sets of conditions have rendered it impossible to produce particles beyond a certain degree of fineness and color.

The percent solution and mixture recommended by the above investigators was first used and then a cell was devised and electrolyte made up as described later in this thesis. The purpose of this investigation was to devise a cell and to formulate an electrolyte which would yield $PbCrO_4$ continuously and maintain a uniform color.

DESCRIPTION OF APPARATUS

A rectangular aquarium jar holding 25 liters of electrolyte was used for the preliminary trials. This did not prove satisfactory because the lead chromate could not be removed immediately upon formation and only short runs could be effected. A large cell was made from a flat bottomed carboy which had a capacity of 40 liters. The bottom was cut off and when inverted formed a cell with a conical bottom. A rubber stopper, to which a rubber and glass tubing had been fastened, was placed in the mouth of the carboy. This formed an outlet for the product without interrupting the operation of the cell.

The carboy was placed in the original container after it had been inverted and supported with four legs about 60 cm. long. The part of the box through which the neck of the carboy protruded was re-enforced to hold the weight of the electrolyte and product made. A platform, connected to the container, was built over the cell to hold the storage tank of electrolyte and the solution of chromic acid. A half-inch lead coil (50 feet long) was placed in the cell to cool or heat the electrolyte as desired.

Two half-inch copper rods were used to conduct the current and to support the electrodes. The electrodes were made of sheet lead and were connected by battery clips to insure a good contact. Each electrode was

placed 1 cm. apart and separated from each other by two glass rods. If they are not separated by the glass rods, they will short and cause cell to cease operating. The switch board was built in with the buss bars and was capable of giving 1200 amperes. 15 volts were used across the bars.

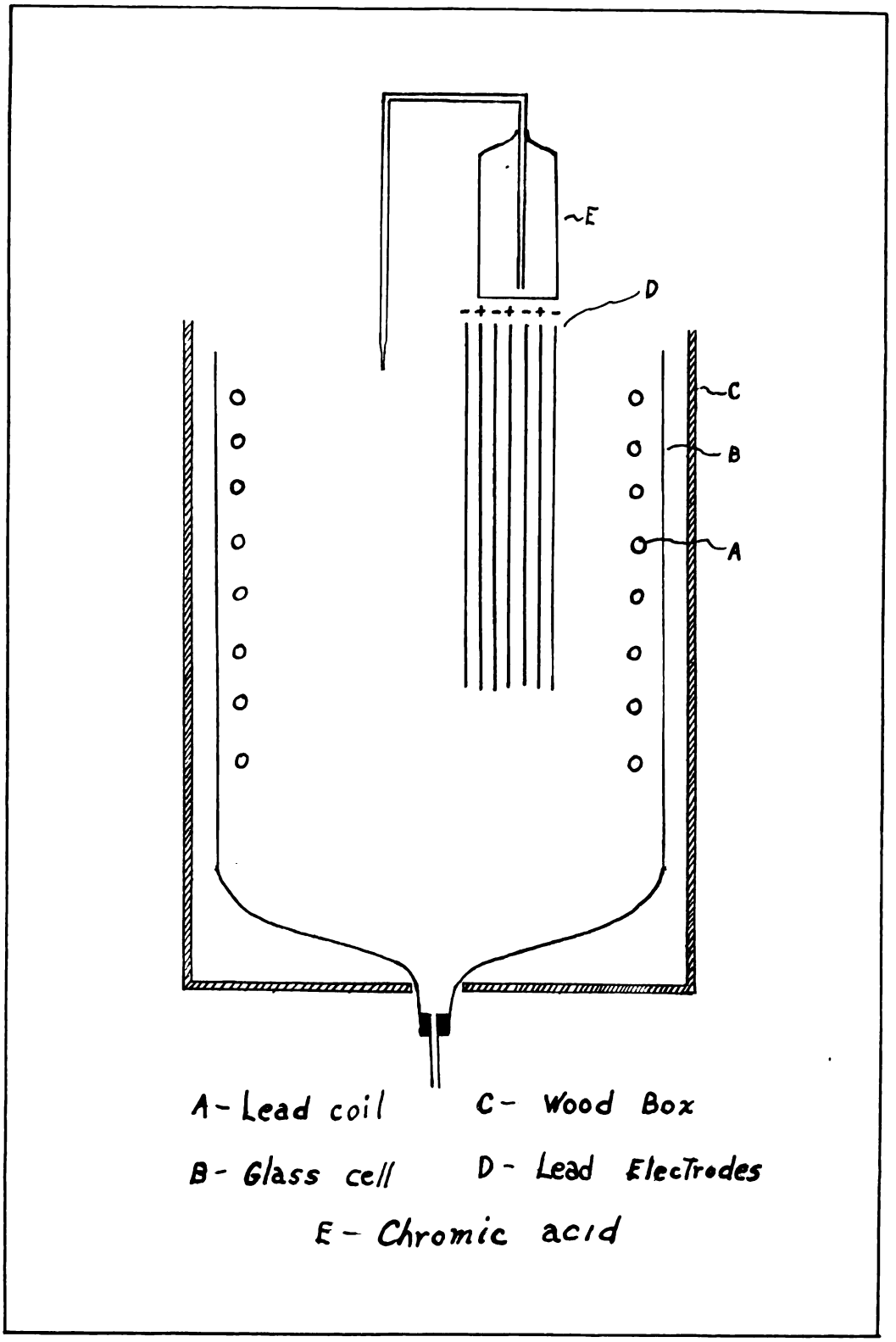

E
D
C
B
A
A - Lead coil
B - Glass cell
C - Wood Box
D - Lead Electrodes
E - Chromic acid

PLATE I

PREPARATION OF THE ELECTROLYTE

In the beginning a 1.5% solution was made, consisting of 20% sodium chromate and 80% sodium chlorate. This gave an electrolyte with a p_H of 8. Experiment showed that the p_H should be below 7. In order to have a common ion and also to lower the cost of the chemicals, the equivalent of sodium acetate was substituted for the sodium chlorate. LeBlanc and Bindschedler showed that equally good results would be obtained with the acetate. Glacial acetic acid was used to correct the p_H to 6.5 or 6.8. To include the acetic acid in the percent solution and to have the percentage of the acetates direct, a correction was made in the percent solution. It is now 1.3% consisting of 23% sodium chromate, 69% sodium acetate and 8% acetic acid. This mixture of salts and acid was made up to the calculated volume with ordinary tap water. Distilled water gave the same results. When a p_H lower than 6.5 was desired, more acetic acid was added; but this addition was not taken into account in the percent solution.

During the operation of the cell the p_H is kept constant by replacing the chromates used and the hydrogen evolved by use of a two molar solution of chromic acid. The chromic oxide was a high grade commercial product. The remainder of the chemicals were of the C.P. quality.

PROCEDURE

The anode electrodes were cleaned mechanically until the metal was bright. This is necessary before each run. The electrodes were suspended on the copper rods in the cell. The electrodes were then connected with battery clips to the copper rod to insure better contact. After the electrolyte was placed in the cell the p_H was checked with the Helige comparator and then corrected to the desired p_H. If the run is to be other than room temperature, the electrolyte is heated by means of the coil through which steam is passed. The chromic acid solution is placed above the cell which is then ready for operation. As the current is passed through the cell, the chromic acid is allowed to drop at a rate to just keep the p_H constant. The p_H is checked at frequent intervals. When the Pb CrO_4 settles to the bottom of the cell, it is drawn off and placed in a storage tank to be washed. Washing is done by decantation. When free of acetates, the chromate is filtered with a suction filter and air-dryed in the room. Weighing was done on a large scales.

TABLE I.

Run No.	p_H	Time hr.	Temp. °C.	Current Density	Total Amperes	Volt	Yield lb.	Current Efficiency	Energy Efficiency	Pounds/ Kilowatt	Color Wet
1.	6.5	5.5	20°	.55	50	2	3.5	96%	5.86%	6.3	Yellow
2.	6.7	6	20°	.6	52	2	4	96%	5.89%	6.4	Yellow
3.	6.5	6	35°	1.1	100	3.5	7.5	94%	3.27%	3.57	Bright Yellow
4.	6.8	4	50°	2.2	200	5	7.75	73%	1.78%	1.94	Yellow
5.	6.8	3	30°	2.2	200	5	7	68%	2.14%	2.33	Yellow
6.	6.5	3	20°	5.5	160	8	5	80%	1.2%	1.3	Yellow
7.	Incomplete										
8.	5.5	3	30°	2	130	5	4.5	85%	2.07%	2.3	Green Yellow
9.	4.5	3	30°	2	130	5	3.6	70%	1.7%	1.84	Green Yellow

1.3% Electrolyte concentration

Composition - 23% sodium chromate, 69% sodium acetate, 8% acetic acid

Run No.	p_H	Time hr.	Temp. °C.	Current Censity	Total Amp.	Volt	Yield lb.	Current Eff.	Energy Eff.	Pounds/ Kilowatt	Color Wet
10.	6.8	2	25°	1.4	80	2.7	2.1	99%	4.47%	4.84	Light Yellow
11.	6.8	3	25o	6	120	7	4.75	99%	1.725%	1.9	Light Yellow
12.	6.8	6	23°	8	160	10	12.5	98.5%	1.2%	1.3	Light Yellow
13.	6.8	4	50°	1.4	80	2.5	4.25	100%	4.88%	5.3	Yellow
14.	6.8	2.5	35°	1.4	72	2.5	2.25	94.4%	4.6%	5.0	Yellow

2.5% Electrolyte concentration

Composition 23% sodium chromate, 69% sodium acetate, 8% acetic acid.

Run No.	p_H	Time hr.	Temp. °C.	Current Density	Total Amp.	Volt.	Yield lb.	Current Eff.	Energy Eff.	Pounds/ Kilowatt	Color Wet
15.	6.8	3	20°	7	140		5.8	99%	Not complete		Light Yellow
16.	6.8	3	20°	1.2	80	2	3	94%	5.7%	6.25	
17.	6.8	2	23°	12	248	8.5	6.5	98.9%	1.41%	1.54	
18.	6.8	1.75	20°	5.3	160	7	4	107%	1.86%	2.04	Dull Green Yellow

Made from waste chromic acid

5% electrolyte concentration

Composition - 23% sodium chromate
69% sodium acetate
8% acetic acid

Run No.	p_H	Time hr.	Temp. °C.	Current Density	Total Amp.	Volt	Yield lb.	Current Eff.	Energy Eff.	Pounds/ Kilowatt	Color Wet
19.	6.5	1	20	16	160	7.5	2.05	97%	1.57%	1.7	Bright Yellow
				Product sticks to electrode							
20.	Run incomplete - Product stuck to electrode										
21.	6.8	2	20	16	160	7.5	4.2	100%	1.6%	1.75	Bright Yellow
22.	6.8	2	20	8	250	3.5	6.25	94.3%	3.29%	3.57	Bright Yellow
23.	6.8	3	20	1.4	80	1.6	3.1	98%	7.47%	8.07	Bright Yellow
24.	6.8	12	20	8	250	3.5	36	90.6%	3.16%	3.42	Bright Yellow & Green Yellow

10% electrolyte concentration

Composition of runs 19 & 20:

23% sodium chromate
69% sodium acetate
8% acetic acid

Composition of runs 21,22,23,24:

12% sodium chromate
82% sodium acetate
6% acetic acid

TABLE II.
Variation with pH

% Solution - 1.3
Composition of electrolyte - 23% Sodium Chromate, 69% Sodium Acetate, 8% Acetic Acid
Temperature - 30°C.

Run No.	Time hr.	pH	Current Density	Total amp.	Volt.	Yield lb.	Current Eff.	Energy Eff.	Pounds/ Kilowatt	Color Wet	Color Dry
5	3	6.8	2.2	200	5	7	80%	2.14%	2.33	Yellow	Light Orange-Yellow
8	3	5.5	2	130	5	4.5	85%	2.07%	2.3	Green Yellow	Light Orange-Yellow
9	3	4.5	2	130	5	3.6	70%	1.7%	1.84	Green Yellow	Light Orange-Yellow

The temperature varied a little during the operation of the cell before the cooling coil was installed. As the p_H was lowered, the color at the time of formation changed from a light yellow to a green yellow. The green color was very pronounced in the electrolyte of 4.5 p_H. However, after being washed and dried, the color of all the trials was very nearly of the same shade. The green color may be due to the formation of chromous acetate which is soluble and easily washes out. The drop in the percent yield in the last run seems to indicate that such a reaction may have taken place. It is better to operate the cell at a p_H of 6.5 to 6.8 since the final color is the same regardless of what the color was when formed.

The change in the concentration of the electrolyte, when the acetic acid is added to change the p_H, was not taken into account. This is only a small amount, and the voltage shows that the conductivity was not raised an appreciable amount.

TABLE III.

Variation with Temperature

p_H of electrolyte 6.8
% solution 2.5
Composition of electrolyte - 23% Sodium Chromate, 69% Sodium Acetate, 8% Acetic Acid
Current Density - 1.4 amp./dm^2

Run No.	Time hr.	Temp. °C.	Volt	Total amp.	Yield lb.	Current Eff.	Energy Eff.	Pounds/ Kilowatt	Color Wet	Color Dry
10.	2	25°	2.7	80	2.1	99%	4.47%	4.84	Light Yellow	Yellow
14.	2.5	35°	2.5	72	2.25	94.4%	4.6%	5.0	Yellow	Light Orange-Yellow
13.	4	50°	2.5	80	4.25	100%	4.88%	5.3	Yellow	Orange-Yellow

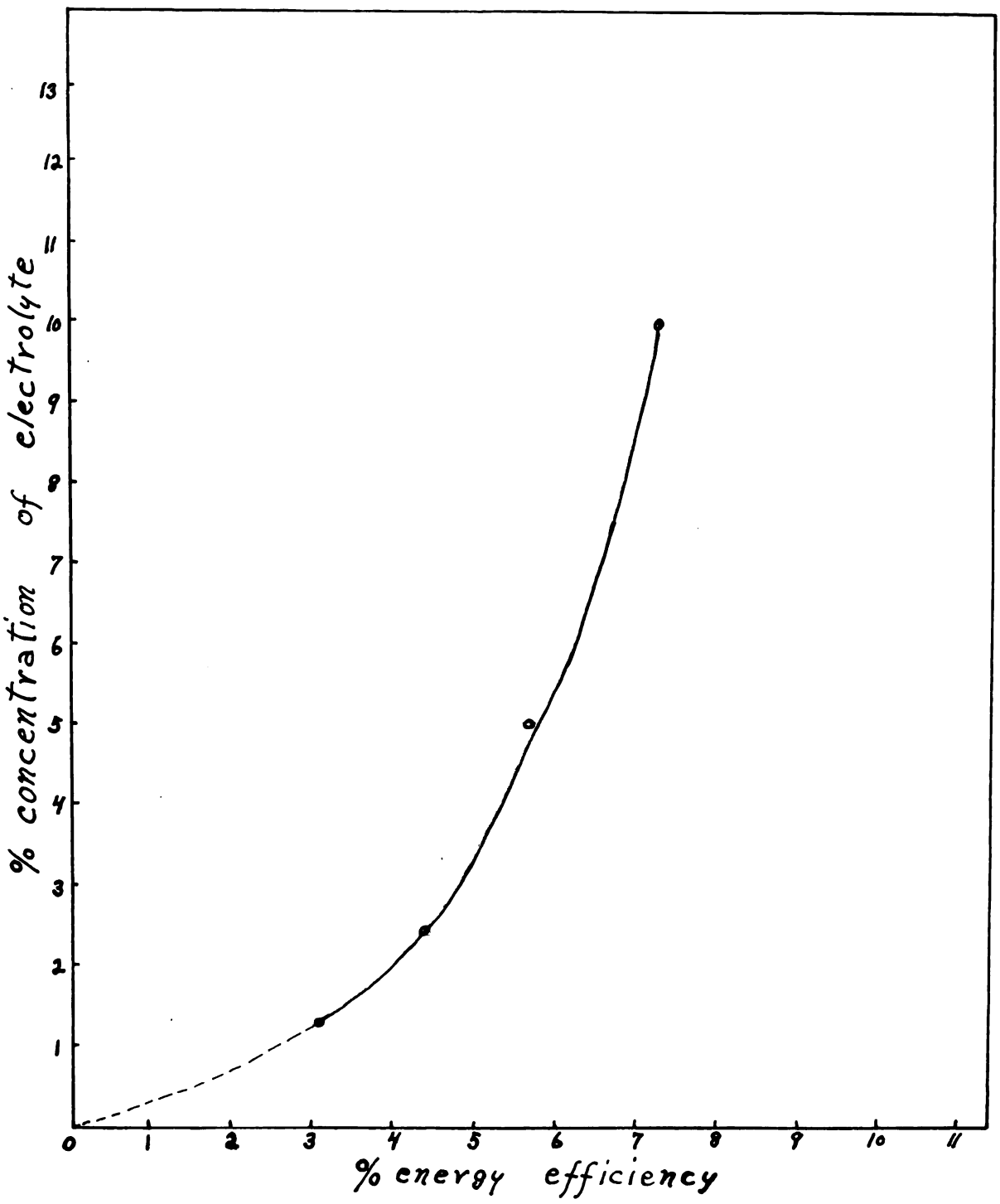
In this series of runs (TABLE III) the temperature was varied from room temperature up to 50°C. The results show a small increase in current efficiency but a darkening of the color. The increase in temperature increases the conductivity and thus shows better results. The change in color is more noticeable when the lead chromate is dry. This gain in energy efficiency is not sufficient to warrant heating the electrolyte to 50°C and the darker color is not as desirable. However, when high current densities are used, the temperature will rise unless cooled. If the color difference did not matter, then it would be better to allow the temperature to rise.

TABLE IV.

Variation with percent solution

p_H of electrolyte - 6.8

Run No.	% Sol.	% Composition Na_2CrO_4	Na Ac	HAc	Time hr.	Temp. °C.	Volt.	Current Dens.	Total Amp.	Current Eff.	Energy Eff.	Pounds/ Kilowatt
3.	1.3	23	69	8	6	35°	3.5	1.1	100	94%	3.27%	3.57
10.	2.5	23	69	8	2	25°	2.7	1.4	80	99%	4.47%	4.84
16.	5	23	69	8	3	20°	2	1.2	80	94%	5.7%	6.25
23.	10	12	82	6	3	20°	1.6	1.4	80	98%	7.47%	8.07



Curve is for current density of 1.4 amp/dm²

Graph I

The percent composition of the electrolyte is the same in all cases except that of the 10% solution. The 10% solution if made like the others as to percentage composition would give the same product and color but would adhere to the electrodes. The amount of chromate must be lessened and so a different composition was made. This gave smoother runs and a product of the same color. Using 8% of acetic acid makes the p_H too low for the 10% solution, so 6% acetic acid was used.

The color or current efficiency does not vary with the change in concentration. The energy efficiency and the pounds per kilowatt are the variables. These more than doubled over the range of the difference in percent of solution. Trials No. 3 and 16 have values slightly higher than have the others at the same current density.

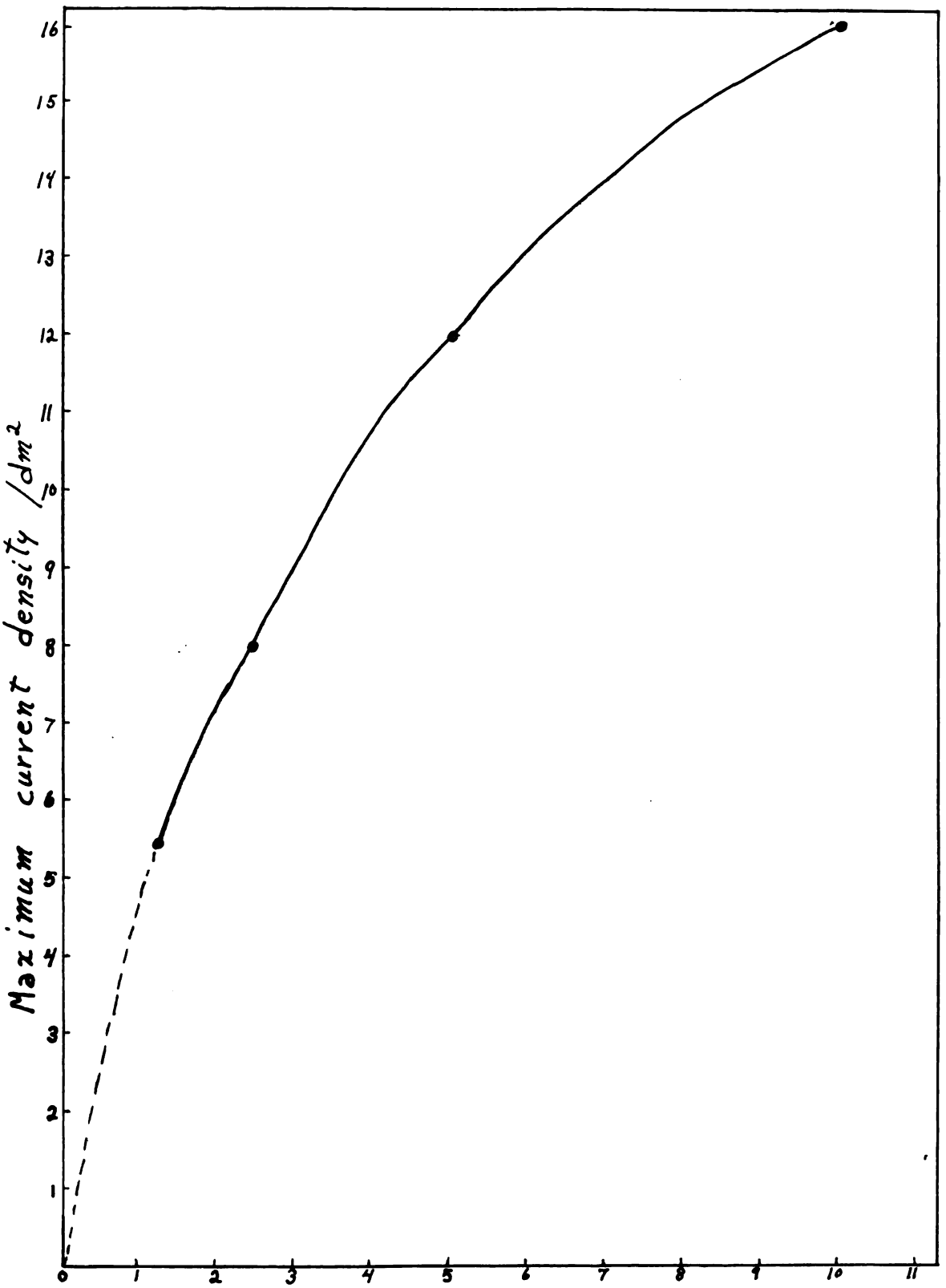
The curve (see Graph I) indicates that over the range from 0% solution to 10% solution, the energy efficiency increases considerable; but that above the 10% solution there will only be a slight rise in the energy efficiency. No runs were made with solutions of more than 10%. However, tests were made to see what the voltage would be for solutions above the 10%. The current density was kept constant and for each concentration the voltage was the same. This would indicate that the

solutions above 10% are not more conductive than the 10% solution. The curve is straightening out and bears out this fact. For the above reason it would not pay to use concentrations above 10%.

TABLE V.

Maximum current density for each concentration

Run No.	% Sol.	% Composition Na_2CrO_4	NaAc	H Ac	Time hr.	Temp. °C	Current Density	Total Amp.	Volt	Yield lb.	Current Eff.	Energy Eff.	Pounds/ Kilowatt
6.	1.3	23	69	8	3	20°	5.5	160	8	5	80%	1.2%	1.3
12.	2.5	23	69	8	6	23°	8	160	10	12.5	98.5%	1.2%	1.3
17.	5	23	69	8	2	23°	12	248	8.5	6.5	98.9%	1.41%	1.54
21.	10	12	82	6	2	20°	16	160	7.5	4.2	100%	1.6%	1.75


Maximum current density /dm²
% concentration of electrolyte
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

Graph II

All attempts to raise the current density above these points for the different percent solutions resulted only in an increase of the voltage. The readings taken are for the lowest voltage at the highest current density. Graph II shows that the current density goes up as the percent of solution is increased. The graph indicates that solutions with a percentage of concentration above 10% will not be appreciably more conductive than the 10% solution. This means that the results shown in the previous graph are arrived at from another point of experiment. The highest percentage solutions are more economical to operate them at the maximum capacity of the cell.

A CONTINUOUS RUN

% electrolyte 10%

% composition 12% Sodium Chromate, 82% Sodium Acetate, 6% Acetic Acid.

Time 12 hr.

Temperature 20°C.

pH 6.5 - 6.8

Voltage 3.5 volts

Current density 8 amp./dm^2

Total amperes 250

Yiels 36 lb.

Current efficiency 90.6%

Energy efficiency 3.16%

Pounds/kilowatt hr. 3.42

This run was made to determine if the cell would work continuously for a long period of time and if a product of the same quality could be obtained. Commercial chromic acid was used for the first 10 hours, and then the acid from a rejected plating bath. The product remained the same for the ten hours; but after the plating acid was used, the particles of $Pb.CrO_4$ did not seem to settle out. It acted like colloidal suspension. The color of the chromate from the used chromic acid was of a green yellow; but after being washed free of all acetates, it was nearly the same shade as that obtained

in the first part of the run. This very clearly showed that the cell would work for an indefinite period of time. The last part of the run showed that the effect of some addition agent would be to cause a finer formation of particles and perhaps a slightly different color. A run was made using the same chromic acid, but the sulfates had been removed. The cell worked in the same way, showing that it was not sulfates which caused the emulsified action.

DISCUSSION

During operation of the cell, the p_H should not be allowed to vary over 0.5 p_H. At low concentration of chromates they are removed if p_H rises and this condition is followed by a formation of spongy lead. If the p_H drops too much, the chromate will adhere to the anodes and cause the cell to cease operating. All work in this thesis was done with the p_H below 7. This does not mean that the cell will not work at a higher p_H. If a p_H above 7 is used, pure lead chromate will not be formed but will yield a mixture of lead chromate and lead oxide.

It is not necessary to use a diaphram in the making of lead chromate. Reduction will not take place at the cathode after the cell has operated for a short time. A coating of chromium chromate forms over the cathode and thus stops all reduction which would tend to take place. Any coarse particles present in the lead chromate can be removed by passing the solution of chromate and electrolyte as it comes from the cell through a cloth of fine weave.

The lead chromate made with the various percent solutions of electrolyte was in a comparatively pure state. The chemical analysis gave a product of over

98% lead chromate. The color was not definitely determined, but it appears that the higher concentrations and the higher current densities give a lighter color and also with more luster. The product becomes finer as the current density and concentration increases. This was determined by mixing a weighed amount of ground $PbCrO_4$ with a definite amount of raw linseed oil. The product which took the most oil was said to be the finest. This may be in error as the fine particles of powder might be agglomerates and thus use less oil.

The product when formed at the anodes did not adhere to the anodes but rolled off in a fine amorphous state. While being washed, and filtered, the product was so fine that it would go through the filter paper until the pores of the paper had become filled. After drying, the lead chromate is in chunks, and must be ground. The state here may be crystalline and thus account for the change in color when drying.

The differences in current efficiency may be accounted for in the product lost in the washing and filtering operations. Because of the large quantity, it was impossible to keep from a constant loss in each procedure. Also, the percentage of moisture present varies. All drying operations were carried out in the air at room temperature.

S U M M A R Y

1. Lead chromate can be made electrolytically in a pure state by controlling the p_H of the electrolyte with acetic acid.
2. The higher current densities and concentrations yield a finer product.
3. A change in color takes place when the lead chromate is dried.
4. An increase in temperature will cause the product to be darker and will also increase the efficiency of the cell.
5. The best results will be had with a 10% solution and a fairly low current density.
6. Cell will work continuously for a long period of time.

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T541 103510
S562 Shulnburg
Electrolytic preparation
of lead chromate.

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