THE PREPARATION OF LEAD ARSENATE ELECTROLYTICALLY

By

WILLIAM WEINER

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CHAPTER I

INTRODUCTION

Lead arsenate was first prepared by Mitscherlich[1], who obtained the orthoarsenate, $Pb_3(AsO_4)_2$, by mixing di-sodium arsenate, Na_2HAsO_4, with basic lead acetate or a neutral lead salt. It was also reported as having been prepared by Berzelius[2], who made it by passing ammonia, NH_3, over lead pyroarsenate, $Pb_2As_2O_7$. Both Mitscherlich and Berzelius claimed that the pyroarsenate was precipitated when an excess of a mixture of lead chloride and lead nitrate reacted in solution with arsenic and di-ammonium arsenate, di-sodium arsenate. Salkowski, who prepared lead arsenate by using lead acetate and di-sodium arsenate later described this compound as a white, easily melted, amorphous powder. On the whole the work of the early investigators was inaccurate and contradicatory.

In 1892 Moulton[3], acting chemist for the Massachusetts Gypsy Moth Commission, first prepared lead arsenate as an insecticide while trying to find a substitute for paris green. Paris green could not be used successfully because it could not be applied in sufficient quantities to kill the moths without injuring the foliage.

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1. Handbuch der Anorganischen Chemie, Vol. XLI, 242(1894).
2. Ibid.
3. Mass. Board Agri. Report, Vol. II, 242(1894).

Smith[1] continued with the work and studied the reactions involved, and matters pertaining to the manufacture of this material. He stated that the spray material is not a single salt but a mixture of the orthoarsenate and di-lead arsenate, the relative amounts depending upon the source of the soluble lead, although temperature and concentrations at precipitation also effected the results. He found that the acetate tends to yield a neutral salt, while the nitrate tends to yield an acid salt.

Fresh lead arsenate is a white, very light flocculent, substance, which has the property of remaining in suspension, for a long period of time, the time of settling depending upon the method by which it is made. The lead arsenate prepared from lead nitrate is more bulky than that prepared from lead acetate and remains in suspension longer. Robinson[2], in determining this ability of twelve commercial brands of lead arsenate, found out that the lead arsenate remaining in suspension after five minutes varied from 1.7 per cent to 90.75 per cent. After being dried out lead arsenate loses some of its bulk and settles out rapidly. Because of this phenomenon it must be packed in air-tight containers, and kept in a moist condition until ready for use. When sprayed it leaves a visible white film on the leaf, a film not easily washed off by rains.

Lead arsenates are used extensively as insecticides,

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1. U.S. Dept. Agr. Bur. of Chem., Bull. CV.
2. Journal of Ind. and Eng. Chem., Vol. XIV, 316(1922).

because of properties which make them adaptable for such a use. They are not entirely satisfactory, but they have advantages over paris green. The advantages of lead arsenate over paris green are:-[1]

1. It is not as injurious to the foliage, as it is much less soluble in water than paris green.
2. It is quite adhesive and not easily washed off by rains.
3. It will remain in suspension longer and is much more easily sprayed.
4. It forms a visible coating that can be readily seen.

It was first thought that lead arsenate was not injurious to the foliage. This is not true as lead arsenate could be, and sometimes is very injurious to the stone fruits, such as peaches, which are very susceptible to insecticides. It has in a few cases caused trees to be entirely defoliated. Many growers refuse to use any insecticide because of the effect they have on the foliage and fruit. O'Gara[2] found that a ten gram sample of badly spotted apple skin contained 0.05 milligrams of metallic arsenic.

Experiments to determine the causes and the amount of injury to the foliage were carried on by the Bureau of Entomology[3] on the department farm at Arlington, Virginia in 1907 and 1908. In 1907 there was no injury to the foliage of the apple trees from any of the mixtures of lead arsenate that they applied, and only a very slight injury to that of

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1. U.S. Dept. Agri. Bur. Chem., Bull. 131, 5(1910).
2. Expt. Station Record (Nov. 1911), Vol.XXV, 642.
3. U.S. Dept. Agri. Bur. Chem., Bull. 131, 5(1910).

the peach trees; none of which injuries were of a decided enough character to attribute it with certainty to the spraying. Some of the trees which had not been sprayed at all showed a condition which would have been attributed to spraying injury if it had not been known that no insecticide had been applied to them. In 1908 there was no damage of the foliage of the apple trees, but the foliage of the peach trees was injured severely. The fruit had a deep red color that extended throughout the flesh, and maturity was hastened about one week. Lead nitrate caused decided injury to the foliage but not the fruit. Lead acetate caused slight injury to the foliage but protected the fruit from insect injury without damaging it.

The fact that there was no injury in 1907, and severe damage of the fruits by lead arsenate in 1908, can be explained by climatic conditions. In 1907 every application was followed by cool cloudy weather, and rain within forty-eight hours. In 1908 every application was followed by cool weather and light rains, but the last application, which caused practically all the damage, was followed by five clear, hot days, and no rain. The dews at night moistened the material and the hot sunshine dissolved the arsenic.

Although lead arsenate will remain in suspension for a long time, some trouble is encountered because of the settling of the arsenate in the spray, especially when knapsack sprayers are used. A great deal of time and money

is wasted because of this. Parker[1] suggested a soap solution, and reported good results in this connection. He also obtained a more even spread of the spray on the surface of the leaves. Lawrence[2] advised the orchardists to try the soap mixture experimentally. The results showed considerable injury to the foliage of the trees in some instances. This injury was due to the soluble arsenic. Tartar and Bundy[3] experimented with soap solutions and found that the solubility of neutral lead arsenate was not increased very much, but the solubility of the acid arsenate was increased appreciably: in one instance being increased 45.82 per cent.

Edwards-Ker[4] advised the use of a one per cent solution, but Robinson[5] advised against the use of soap solutions unless the effects of such solutions were tried experimentally under the same conditions that they are to be used, as climatic conditions have a great deal to do with the effect of lead arsenate and lead arsenate soap solutions.

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1. Journal of Ind. Eng. Chem., Vol. V, 561(1913).
2. Ibid.
3. Ibid.
4. Expt. Sta. Record, Vol. XXXIII, 538(1915).
5. Journal Of Ind. Eng. Chem., Vol. XIV, 315(1922).

CHAPTER II

PURPOSE OF INVESTIGATION

The primary purpose of this investigation is to devise a process by which lead arsenate can be produced at a cost lower than that of the present day processes.

The secondary purpose of this investigation is to devise a process that would do away with the complex methods by which lead arsenate is prepared today:-

1. By avoiding the use of lead nitrate which has to be made by dissolving lead in nitric acid. When lead is dissolved in nitric acid obnoxious nitric acid fumes are given off. The preparation of lead nitrate also requires the use of expensive apparatus.
2. By avoiding the use of lead acetate which is made by a complex method involving the use of chambers and pressure.[1]
3. By avoiding the preparation of lead arsenate by fusing any oxide of lead with arsenious or arsenic oxide.[2]

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1. German Patent 173,521(1904); U. S. Patent 1,097,099(1914).
2. U. S. Patent 929,962(1909).

CHAPTER III

METHOD OF PREPARATION TODAY

Lead arsenate is prepared today by mixing either lead nitrate, $Pb(NO_3)_2$, or lead acetate, $Pb(C_2H_3O_2)_2$, with disodium arsenate, Na_2HAsO_4, or by roasting lead oxide with arsenious oxide, As_2O_3, or arsenic oxide, As_2O_5, or any soluble arsenate.

Most of the lead arsenate is prepared by mixing either lead nitrate or lead acetate with sodium arsenate. There is little difference in the expense of either of the methods, the production of lead arsenate from lead nitrate being slightly cheaper because a little less lead is needed to make the same amount of lead arsenate.

Haywood[1] in his investigations came to the conclusion that the reactions take place as follows:-

$$3\ Pb(C_2H_3O_2)_2 + 2\ Na_2HAsO_4 \longrightarrow Pb_3(AsO_4)_2 + 4NaC_2H_3O_2 + 2\ HC_2H_3O_2$$

$$Pb(NO_3)_2 + Na_2HAsO_4 \longrightarrow Pb\ HAsO_4 + 2\ NaNO_3$$

The above method of preparing lead arsenate can be used by the orchardists cheaply at the place where the insecticide is to be employed without the use of costly apparatus; that is, if the reacting chemicals can be obtained at a reasona-

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1. Twenty-fourth Ann. Report, Mass. Agr. Exp. Sta. Record.

ble price. A formula can be obtained from the government. The government bulletins and scientific magazines also publish formulae from time to time.

In these formulae a great deal of attention is paid to the manner of mixing the ingredients. Some formulae specify a certain definite amount of water while others will specify twice and sometimes three or four times that amount of water. A certain formula will state that the ingredients should be mixed dry and then water added, while others will advise the dissolving of the ingredients before mixing, but not one formula advises the use of an excess of soluble lead salt, nor do they explain how to test for an excess of soluble lead. Minor points are overemphasized and important points are overlooked as in the majority of formulae. An excess of soluble lead is absolutely essential, because that will cut down the amount of soluble arsenic that is very injurious to the plants.

There are several patents for the production of lead arsenate. These processes used by various manufacturing concerns are generally cheaper than the production from lead acetate or lead nitrate. These processes generally involve the use of a lead salt or oxide and the arsenious or arsenic oxide, or a soluble arsenate. One company has the patent rights to a method involving the use of lead oxide in a solution of a soluble arsenate[1], while another

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1. U. S. Patent 1,172,741(1916).

company has the patent rights to a method of roasting white arsenic and a lead compound in the presence of oxygen or an oxidizing agent. These methods, while better than the preparation by lead nitrate or lead acetate are still inefficient, since they involve the use of heat, one of the most wasteful forms of energy.

Brown, Voris, and Henke[1], investigated the preparation of lead arsenate by roasting arsenous oxide and litharge. The charge to be roasted was placed in a jar and heated to the desired temperature, the jar being turned in a rotary motion. A current of air was circulated through the jar and it was placed in a closed furnace. A loss of arsenic could be noticed by odor and fumes that were given off for a short time. The material in the jar formed a brittle slag-like substance which at first had a yellowish-gray color. The lumps were ground by pebbles in the rotating jar and the substance soon turned white (when the proper proportions were used). Samples were taken from the furnace at definite periods of time during the roasting and analyzed for arsenic pentoxide, arsenious oxide and soluble arsenic. Temperatures varying from 300-500°Centigrade were used. The best results were obtained at 450°Centigrade. Practically all the arsenic was changed to As_2O_5 in three hours and the percent of soluble arsenic as As_2O_5 was 0.318.

Tartar and Grant[2] prepared lead arsenate electroly-

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1. Journal of Ind. and Eng. Chem., Vol. XIII,531-33(1921)
2. Ibid., Vol. XIV, 311-313(1922).

tically. They reported 99.5 per cent current efficiency. The cell consisted of a jar in which the lead electrodes were dipped into a mixture of 0.05 per cent di-sodium arsenate and one to two per cent sodium chlorate. They used a current density of 1.25-1.875 amperes per square decimeter and a current of approximately one ampere.

Ormont[1] recently devised a method for the electrolytic preparation of lead arsenate. He reported a 97 per cent current yield, and an average energy efficiency of one kilogram per kilowatt hour. The cell consisted of a nickel cathode, a lead anode, and a diaphragm of vegetable parchment. The anolyte consisted of an alkali arsenate that was neutralized with acetic acid and the catholyte was a 15 per cent solution of sodium hydroxide or sodium salt.

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1. Ukranski Khem. Zhurnal, Vol. II(1926).

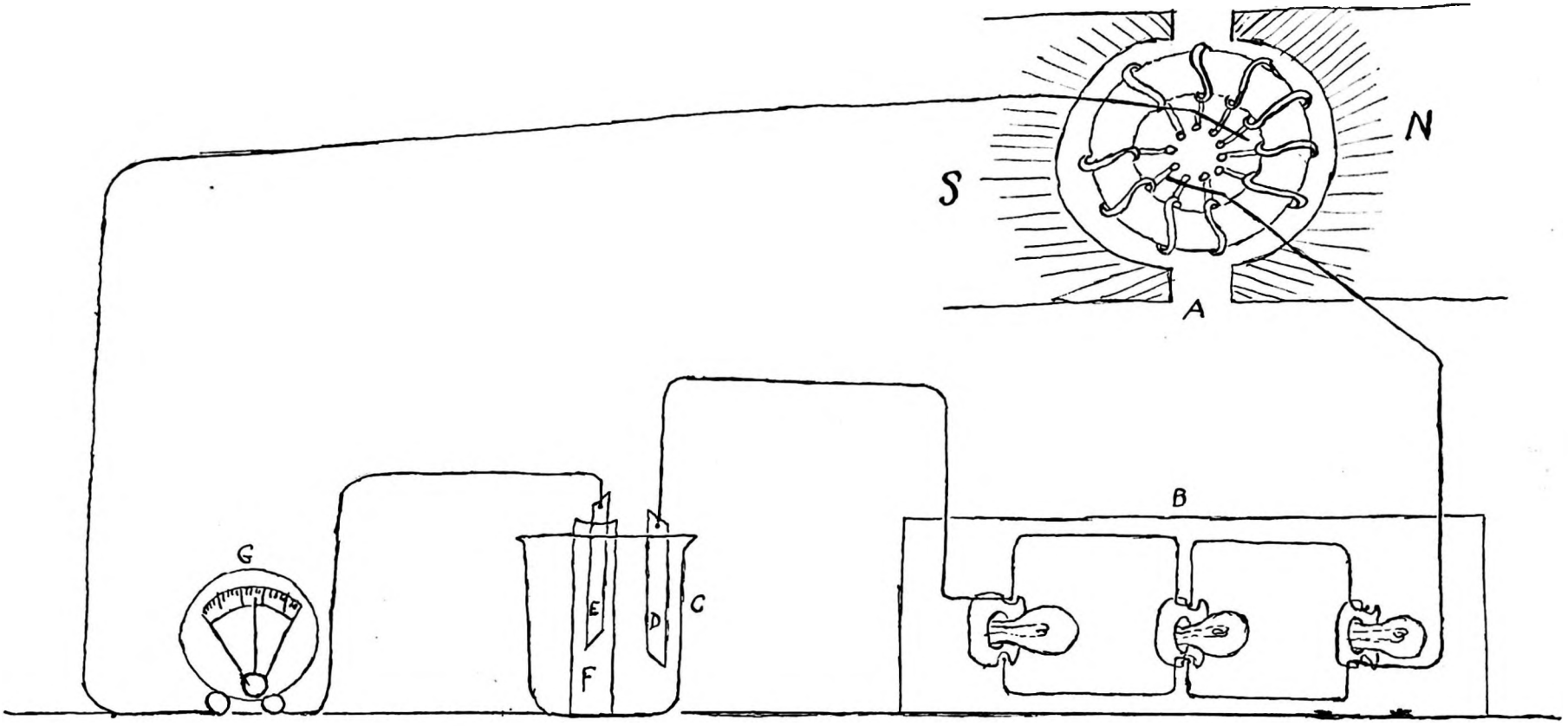

DIAGRAM OF APPARATUS

A- D.C. generator
B- Resistance board
C- Liter beaker
D- Lead anode
E- Sheet iron cathode
F- Porous cup
G- Ammeter

CHAPTER IV

DESCRIPTION OF EXPERIMENTS
EXPLANATION

The apparatus consisted of a liter beaker containing an electrolyte, 600 cubic centimeters of $KClO_3$, in which a lead anode was dipped, and a cathode of sheet iron that was dipped in a 200 cubic centimeter solution of Na_3AsO_4. The anode was separated from the cathode by a porous cup. This cell was connected to a resistance board and an ammeter which were in turn connected to a source of direct current. The concentrations have not been discussed here because, as it will be noted later, they have been varied.

This method of preparation of lead arsenate differs from that of Tartar and Grant in the fact that the anode was separated from the cathode by a porous cup. The method in which the porous cup was employed permits the use of a higher concentration of Na_3AsO_4 than has been used before.

After the solutions were placed in the cell the current was turned on for a definite length of time, that length of time being calculated from Faradays' laws.

The passage of an electric current through an electrolyte decomposes it, the positive radical of the electrolyte appearing at the negative electrode, the negative radical at the positive electrode[1].

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1. Kendall, James, General Chemistry, p. 262.

In 1834 Faraday[1] began a systematic investigation of the chemical effect upon an electrolyte produced by an electric current. His object was to determine the quantitative effect of the passage of a current through an electrolyte. The results of his experiments gave rise to the two laws which are the basis of the science of electrochemistry and all electrochemical reactions. The laws of electrolysis are[2]:-

1. The resulting chemical effect is directly proportional to the product of the current into the time of electrolysis, that is, to the quantity of electricity which has flowed through.
2. This quantity is in all cases proportional to the equivalent weights of the substances concerned.

Faraday's first law states the relation between the quantity of electricity and the quantity of any particular substance set free or taking part in any electrolytic process, a faraday (96,540 coulombs) depositing or taking up one gram atomic weight of any monovalent substance. If a substance is di-valent or tri-valent it will take either two or three faradays depending upon the valence.

With the knowledge of Faraday's laws, the length of a run can be determined in advance in the following manner;

1. The weight of the sodium arsenate used being known, the weight of lead necessary to react with it was determined.
2. The amount of current necessary to dissolve that weight of lead was calculated.
3. The amperage being determined, the length of the

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1. Moore, F.J., A History of Chemistry, p. 146.
2. Allmand, A. J., and Ellingham, H. J. T., The Principles of Applied Electrochemistry, pp. 14-15.

run was calculated by dividing the coulombs required by the amperes.

Determination of the length of a run.

Sample Calculation

Assuming that we have one gram of sodium arsenate, determine the time necessary to dissolve enough lead required to react with the sodium arsenate.

$$3\ Na_3AsO_4 + 5Pb + 10\ H_2O \longrightarrow Pb_5OH(AsO_4)_3 + 9\ NaOH + 5\ H_2$$

$$3\ Na_3AsO_4 \rightleftharpoons 5\ Pb$$

$$621:1 = 1036:X$$

$$621\ X = 1036$$

$$X = 1.6683 \text{ gms. } Pb \rightleftharpoons 1 \text{ gm. } Na_3AsO_4$$

$$207.2:1.6683 = 2^{\circ}96,540:X$$

$$207.2\ X = 344,115.364$$

$X = 1684.05$ coulombs necessary to convert 1gm. Na_3AsO_4 to basic lead arsenate.

With a current of one ampere the time necessary for the run will be:

$$1684.05 \times 60 = 26 \text{ min. } 40 \text{ sec.}$$

When the run was completed the sample was filtered and the precipitate was dried and weighed. The precipitate was then analyzed to determine the per cent lead. The percentage of arsenic was sometimes determined as a check. The following method of analysis was used:-[1]

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1. Griffin, R. C., Technical Methods of Analysis, P. 68.

One gram of dry powder was dissolved in 30 cubic centimeters of HNO_3 (diluted with four times its volume of water) on a steam bath. This was then transferred to a 250 cubic centimeter volumetric flask, cooled to room temperature and diluted to the mark. Fifty cubic centimeters of this solution was pipetted and diluted to at least 400 cubic centimeters heated to boiling and dilute HNO_3 (1:10) was added to redissolve the precipitate. Fifty cubic centimeters of a hot 10 per cent solution of $K_2Cr_2O_7$ was slowly added; it was boiled for three minutes and filtered hot. The yellow crystals of $PbCrO_4$ were dried and weighed and the percent of lead in the sample determined.

The percentage of arsenic was determined by transferring 100 cubic centimeters of the prepared lead arsenate in nitric acid to a porcelain dish. Six cubic centimeters of concentrated sulfuric acid was added, and the solution evaporated to a syrupy consistancy on a water bath, and then on a hot plate, till white fumes were given off, a little water added, and then again evaporated till white fumes were given off. The syrup was cooled, and diluted to 100 cubic centimeters, of which 50 cubic centimeters was used for analysis. It was transferred to a 400 cubic centimeter Erlemeyer flask, and 50 cubic centimeters of water added to it. One gram of KI crystals were added, the solution boiled till it was colorless (with volume above 50 cubic centimeters), cooled under running water, diluted to about

200 cubic centimeters, and a drop or two of 0.1 Normal $Na_2S_2O_3$ added till the iodine was just dissolved. Powdered Na_2CO_3 was added to the solution until it was basic; it was made acid with H_2SO_4, and then made alkaline with an excess of $NaHCO_3$. It was then titrated with 0.05 Normal iodine and the per cent of arsenic in the lead arsenate calculated.

Sample calculation

1.Lead determination

Assuming that a one gram sample of lead arsenate gave 0.2192 grams of $PbCrO_4$.

We multiply this number by five, since one fifth of the original solution was used in the precipitation of lead.

$$0.2192 \times 5 = 1.069$$

To get the amount of lead we use the proportion

$$323.31 : 1.0690 = 207.2 : X$$

$$323.31\ X = 221.4968$$

$$X = 0.6855 \text{ grams Pb in sample.}$$

$$\therefore\ 0.6855 \times 100 = 68.55\% \text{ Pb.}$$

2.Arsenic determination

Let us assume that 0.81 cc. I_2 reacted with the arsenic solution.

We multiply by five as one fifth of the original solution was used in the determination.

$$0.81 \times 5 = 4.05 \text{ cc. of } 0.05 \text{ N. } I_2 \text{ necessary to react with 1 gram lead arsenate.}$$

$$As_2O_3 + 4\ NaOH + 2\ I_2 \longrightarrow$$

$$As_2O_5 + 4\ NaI + 2H_2O$$

$$As \eqsim 2\ I_2$$

1 cc. 0.05 N. I_2 contains 0.127 grams I_2

0.127 grams $I_2 \eqsim$ 0.0375 grams As

0.0375 X 4.05 = 0.1519 grams as in sample.

0.1519 X 100 = 15.19% as in sample.

The formula of lead arsenate can be determined from the percentages of lead and arsenic, but it is not necessary to do that because it has already been done by other investigators and their results can be found in literature on lead arsenate.

CHAPTER V

DESCRIPTION OF EXPERIMENTS (CONTINUED)
RESULTS

The effect of the concentration of Na_3AsO_4 on the yield was the first to be investigated. Solutions of concentrations varying from two per cent to one-fourth of one percent Na_3AsO_4 were used in this experiment to determine the concentration of Na_3AsO_4 that gave the maximum yield.

TABLE I

Run	Concentration of $KClO_3$	Concentration of Na_3AsO_4	Current	Weight of ppt.
1	2%	2%	0.9 Amp.	trace
2	2%	1%	1 "	1.030 gms.
3	2%	0.5%	1 "	1.7783 "
4	2%	0.25%	1 "	0.8405 "

Four runs were made to determine the effect of the concentrations of sodium arsenate on the yield. The concentration of $KClO_3$ was kept constant and the current was kept as constant as possible, but the concentration of Na_3AsO_4 was changed. A two per cent solution of Na_3AsO_4 gave only a trace of precipitate, a one per cent solution gave an increase in the amount of precipitate, a 0.5 per cent solution gave a still further increase in the yield, but when a 0.25 per cent solution was used the amount of precipitate in the yield dropped. From these results of table 1 it is evident

that the best yield will be obtained with a 0.5 per cent solution of Na_3AsO_4. On analysis the precipitate was found to contain more than 90 per cent lead and only a trace of arsenic.

Mr. Kennedy thought that the high percentage of lead was due to the low current density at the anode, and suggested the increase of the current density at that electrode. The following experiments were made to see if the current density had any effect on the percentage of lead in the precipitate. The concentration of the Na_3AsO_4 was again varied to verify the results of the previous experiments. The effect of stirring was also investigated.

TABLE II

Run	Conc. of $KClO_3$	Conc. of Na_3AsO_4	Current	Current density at anode	Wt. of ppt.	% lead
5	2%	0.25%	1 amp.	0.38 amp./dm.^{2}	0.4026 gm.	75.45
6	2%	0.25%	0.9 "	1.223 "	0.4134 "	71.2
7	2%	0.5%	0.98 "	1.8672 "	0.9452 "	68.02
8	2%	0.5%	0.98 "	1.9255 "	0.8327 "	67.93
9	2%	1%	0.98 "	1.8032 "	1.4894 "	68.5
10	2%	1%	0.98 "	1.4078 "	1.3963 "	70.1

The results of the above experiments proved that the high percentage of lead in the first, second, third and fourth runs was due to the low current density at the anode, for as soon as the current density at that electrode was increased,

the percentage of lead in the precipitate was decreased, and the percentage of arsenic was increased. The best result, a percentage of 70.1 for lead - approximately the theoretical value for lead in $Pb_5OH(AsO_4)_3$ - was obtained with a current density of 1.4078 amperes per square decimeter at the anode. The per cent of lead was decreased when the current density was increased, and increased when the current density was decreased.

The $KClO_3$ solution was stirred continually during the sixth, seventh, and ninth runs. There was no stirring during the fifth, eighth and tenth runs. A slightly greater yield was obtained when the solution was stirred. A much finer precipitate was also obtained when the solution was stirred.

A maximum efficiency was again obtained with a 0.5 per cent solution. The current efficiencies have not been tabulated up to this time, because they have not been very high (below 50%)

The effect of the concentration of $KClO_3$ and mixing the liquids after the run was completed was next investigated.

TABLE III

Run	Conc.of $KClO_3$	Conc.of Na_3AsO_4	Current	Current density at anode	% Lead
11	3%	0.5%	0.98 amp.	1.351 amp./dm.^{2}	69.8
12	2%	0.5%	1.05 "	1.667 "	70.23

Run	Wt. of ppt.	Current efficiency
11	2.1613 gms.	91.42%
12	2.3575 "	99.67%

A three per cent solution of $KClO_3$ was used in the eleventh run. When the run was completed the solutions were allowed to stand for forty-eight hours, so that the solutions had time to diffuse completely through the porous cup. The lead arsenate precipitated out in white plate-like crystals and the yield was increased enormously. The current efficiency of the run was 91.42 per cent.

A two per cent solution of $KClO_3$ was used in the twelfth run. Instead of allowing the solutions to diffuse through the porous cup, when the run was completed, the liquid from the porous cup was immediately poured into the beaker. A white flocculent precipitate, that had the characteristics of lead arsenate was formed immediately, and settled slowly. The current efficiency of this run was 99.67 per cent.

The effect of a 2 per cent solution of Na_3AsO_4 on the efficiency of the run was again investigated. The solution in the porous cup was again mixed with that in the beaker. This run was made to determine if the loss in efficiency

of the solution at this concentration was very great, as it is more economical to work with higher concentrations in a commercial plant.

TABLE IV

Run	Conc.of $KClO_3$	Conc.of Na_3AsO_4	Current	Current density at anode	Wt. of ppt.
13	2%	2%	.95 amp.	1.3158 amp./dm.^{2}	8.1432 gms.

Run	% Lead	Current efficiency
13	70.5	86.71%

The current efficiency of this run is fairly high (86.71 per cent), but it is quite a bit lower than that of the twelfth run. The same white flocculent precipitate that was obtained in the twelfth run was produced in the thirteenth run.

CHAPTER VI

SUMMARY OF RESULTS

The best results (99.67 per cent current efficiency) were obtained with 200 cubic centimeters of 0.5 per cent Na_3AsO_4 in the porous cup, 600 cubic centimeters of a 2 per cent $KClO_3$ in the beaker, a current of approximately one ampere, and a current density, at the anode, of approximately 1.4 amperes per square decimeter. Some lead arsenate was precipitated during the run, but most of it was precipitated when the solutions were mixed after the current was turned off. Under these conditions the lead arsenate produced would be $Pb_5OH(AsO_4)_3$.

This method of producing lead arsenate has one advantage over the method devised by Tartar and Grant. Greater concentrations of sodium arsenate can be used in this method. Tartar and Grant had to work with very low concentrations (0.05 per cent Na_2HAsO_4), but in this method a 0.5 per cent solution gives the maximum current efficiency. A 2 per cent solution also gives a high current efficiency, but it is lower than that obtained with a 0.5 per cent solution.

CHAPTER VII

CONCLUSIONS

Although higher concentrations have been used in this method of producing lead arsenate than have been used by Tartar and Grant, there is no way of telling definitely whether lead arsenate can be produced efficiently in this way, because the energy efficiency has not been determined.

Another important factor in commercial processes is the quantity that can be used in each run,and only 200 cubic centimeters of sodium arsenate was used each time. Increased volumes of Na_3AsO_4 and $KClO_3$ in the ratio of 1:3 would most likely give the same results, but a change in this ratio might affect the quantity of the yield.

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