

# Electrolytic Reactions of Naphthalene and its Derivatives. Part III. Electrolytic Oxidation of $\alpha$ -Naphthylamine and ar-Tetrahydro- $\alpha$ -Naphthylamine

BY

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## (I) ELECTROLYTIC OXIDATION OF $\alpha$ -NAPHTHYLAMINE.

The electrolytic oxidation of the aromatic compounds containing the amine group has been studied by Goppelsröder and others.<sup>1</sup> They obtained aniline black from aniline and complex colouring matter from other aromatic amines as the chief oxidation products. Sometimes oxidation was observed by them to progress still further so as to change the aromatic amines into the quinone compounds, as in the case of aniline<sup>2</sup> from which p-benzoquinone was produced.

As to the electrolytic oxidation of  $\alpha$ -naphthylamine there is apparently no other record in chemical literature than the work of Goppelsröder<sup>3</sup> who is reported to have obtained naphthylamine-violet. So I have taken up the problem and undertaken to study the progress of the oxidation reaction, in the expectation that it would give some interesting result when compared with the oxidation reactions of naphthalene and  $\alpha$ -naphthol previously investigated by me<sup>4</sup>.

$\alpha$ -Naphthylamine is known to give naphthamein when chemically oxidized by ferric chloride or silver nitrate,<sup>5</sup> and  $\alpha$ -naphthoquinone by

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<sup>1</sup> Goppelsröder, C. R., **81**, 944; **82**, 331,1199 (1875); Coquillion, *ibid.*, **81**, 408; **82**, 228 (1875); W. Löb, *Electro-chemistry of organic compounds*, 195, (1906).

<sup>2</sup> Elbs, *Chem-Ztg.*, **17**, 210; D.R.P. 172654 (1903).

<sup>3</sup> *Loc. cit.*

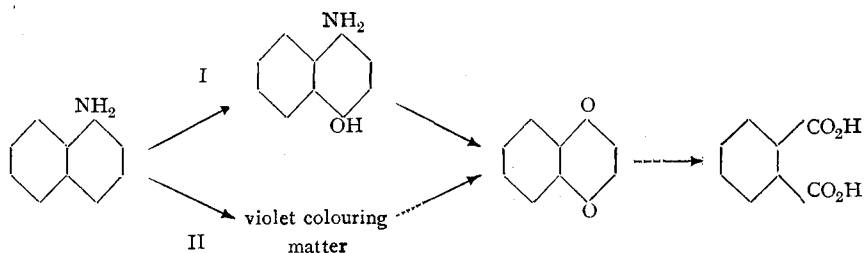
<sup>4</sup> These memoirs, **5**, 111,263 (1921).

<sup>5</sup> Piria, *Lieb. Ann.*, **78**, 64 (1851); Schiff, *ibid.*, **101**, 92 (1857); **129**, 255 (1865).

potassium bichromate<sup>1</sup> or lead-peroxide<sup>2</sup> in a sulphuric acid solution. According to my experiments described below, electrochemical oxidation gives an analogous result producing a violet colouring matter and  $\alpha$ -naphthoquinone as the oxidation product.

As the anode material, platinum, graphite and lead-peroxide were used, of which lead-peroxide gave the best results (Table I). Contrary to the aniline which is solely transformed into aniline black when electrolysed with a platinum electrode<sup>3</sup>  $\alpha$ -naphthylamine was found always to produce  $\alpha$ -naphthoquinone. This is due to the fact that the violet colouring matter first produced is soluble in acetone used as solvent, while aniline black is insoluble in it. As is evident from table 2, up to about 9 times of the theoretical electric quantity, the increase of the current quantity and that of the production of  $\alpha$ -naphthoquinone run parallel. The current yield of the product was observed to become the smaller the greater the current density, the maximum yield having been attained at about 1 amp. per 100 sq. cm. (Table 3). The elevation of the electrolytic temperature does not necessarily favour the yield (Table 4). The suitable concentration of sulphuric acid was 10—30%, and especially was the 10% solution found the best (Table 5). As the oxygen-carriers the following substances were found to act effectively:—potassium chromate, chrome-alum, potassium chlorate, and ferric sulphate, etc. (Table 6).

$\alpha$ -Naphthylamine may be assumed to change into  $\alpha$ -naphthoquinone by electrochemical oxidation in two different ways, that is, it will first be transformed into amidonaphthol on the one hand and into violet colouring matter on the other, as is shown in the following scheme:



<sup>1</sup> P. Monnet, F. Reverdin and E. Noeltig, Ber. D. chem. Ges., 22, 2036 (1879).

<sup>2</sup> K. Ono, not yet published.

<sup>3</sup> A. Moser, Die Elektrolytischen Prozesse der org. chem., 68 (1910).

The progress of reaction II was exactly traced in my experiments, so I endeavoured to seize amidonaphthol as the intermediate product and to confirm the fact that reaction I really occurs; but all trials failed. Perhaps it would be instantly further oxidized into the corresponding quinone as soon as it is produced, being very unstable toward the oxidizing action.

(2) ELECTROLYTIC OXIDATION OF AR-TETRAHYDRO- $\alpha$ -NAPHTHYLAMINE.

It is known that ar-tetrahydro- $\alpha$ -naphthylamine gives a colouring matter like naphthamine by the action of ferric chloride, chromic acid etc.<sup>1</sup> and ar-tetrahydro- $\alpha$ -naphthoquinone<sup>2</sup> by a sulphuric acid solution of potassium bichromate. I have also obtained ar-tetrahydro- $\alpha$ -naphthoquinone by oxidizing it electrolytically. As the anode material, platinum, lead-peroxide and graphite were used, of which lead-peroxide gave the best result (Table 7). The current density at about 1 amp./100 sq. cm. was found the best (Table 9). The most suitable temperature was 18—23° C (Table 10). The concentration of sulphuric acid should be maintained between 10 and 30% (Table 11). As the oxygen-carrier chrome compound and potassium chlorate, etc. acted effectively (Table 12).

EXPERIMENTAL PART.

(1) ELECTROLYTIC OXIDATION OF  $\alpha$ -NAPHTHYLAMINE.

(a) PRELIMINARY EXPERIMENT.

$\alpha$ -Naphthylamine recrystallized from dilute alcohol and melting at 50° was used.

1. The anode liquid consisting of 100 c.c. sulphuric acid (20%), 50 c.c. of acetone and 1 gram of  $\alpha$ -naphthylamine, was introduced into a beaker. A porous cell, successively washed with 1% alkali, water, 5% hydrochloric acid and water, was placed in it as the cathode compartment. Sulphuric acid (20%) was taken as the cathode liquid, and a perforated lead plate coated with lead-peroxide about 10.0 × 8.0 cm. served as the anode, and a smaller sheet of lead as the cathode. The beaker was cooled with water to keep the

<sup>1</sup> Bamberger, Ber. D. chem. Ges., **22**, 775 (1889)

<sup>2</sup> Bamberger and Lengfeld, *ibid.* **23**, 1131 (1890)

temperature of the bath always at about 20°. Electrolysis was continued for nearly 2 hours with a current of 0.8 ampère.

After electrolysis, the anode liquid was extracted with ether. A violet precipitate insoluble both in an acetone-ether mixture and in water solution, was produced. The precipitate was filtered and washed several times with warm dilute alcohol. The ethereal extract was evaporated, and the residue was subjected to steam distillation. The yellow crystalline distillate, after having been dried, was recrystallized from petroleum ether, whereupon yellow needle crystals, melting at 125° were obtained. The yellow crystals were proved to be  $\alpha$ -naphthoquinone by a direct comparison with a pure specimen.

$\alpha$ -Naphthoquinone isolated as above was analysed with the following results:

0.1862 gr. substance gave 0.5153 gr. CO<sub>2</sub> and 0.0665 gr. H<sub>2</sub>O

	Found	Cal. (C <sub>10</sub> H <sub>6</sub> O <sub>2</sub> )
Carbon	75.43	75.93
Hydrogen	3.96	3.83

2. In the second experiment electrolysis was continued for nearly 3 hours with a current of 1.6 ampère under the same conditions as before. The yellow crystals identified as  $\alpha$ -naphthoquinone by the colour reaction and by a direct comparison with a pure specimen were obtained on distilling the anode solution with steam. The distillation residue was extracted with ether, and the ethereal extract was washed several times with a saturated sodium carbonate solution. The alkaline liquid thus obtained was neutralized with dilute hydrochloric acid and again extracted with ether. After drying with anhydrous sodium sulphate, the ethereal extract was evaporated and the residue was sublimed. A sublimate, identified as phthalic acid anhydride by the fluorescence reaction, was procured.

#### (b) QUANTITATIVE INVESTIGATION.

Having now confirmed the fact that  $\alpha$ -naphthylamine can be oxidized into a violet colouring matter,  $\alpha$ -naphthoquinone and phthalic acid, I next attempted to examine the oxidation reaction under various conditions quantitatively. In all experiments I took care to work at a definite current concentration and temperature.

##### 1. Influence of the anode material.

Anode solution: 1.0 gr.  $\alpha$ -naphthylamine

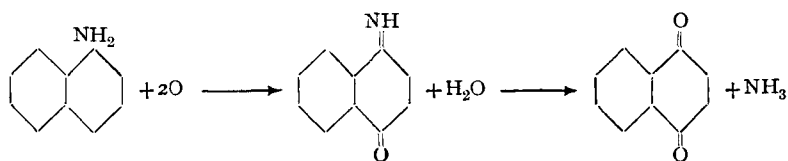
50 c.c. acetone  
 100 c.c. H<sub>2</sub>SO<sub>4</sub> (20%)  
 Cathode solution: H<sub>2</sub>SO<sub>4</sub> (20%)  
 Temperature: 18–23°.

TABLE I.

Anode		Cathode	Current strength	Voltage	Current quantity	α-naphthoquinone	Current yield of α-naphthoquinone	Material yield of α-naphthoquinone
Material	Surface area							
Platinum	40.0	Spiral platinum Lead	0.8	3.2–3.4	1.6	0.0097	0.41	0.87
Lead peroxide	80.0		0.8	2.8–2.9	1.6	0.5643	23.97	51.07
Graphite	45.0	Spiral platinum	0.9	2.6–2.7	1.8	0.0063	0.23	0.57

The anode liquid introduced into a porous cell was constantly agitated by a rapidly revolving stirrer.

After electrolysis the anode liquid was extracted with ether. The solvent was then distilled off and the residue was subjected to steam distillation. α-Naphthoquinone obtained thus was collected in a Gooch crucible, dried and weighed. The current yield was calculated on the assumption that oxidation takes place according to the following equation:



2. Influence of current quantity.

Anode solution: 1.0 gr. α-naphthylamine

50 c.c. acetone

100 c.c. H<sub>2</sub>SO<sub>4</sub> (20%)

Anode: Lead peroxide (80.0 sq. cm.)

Cathode solution: H<sub>2</sub>SO<sub>4</sub> (20%)

Cathode: Lead

Current density: 0.02 ampère per 1 sq. cm.

Temperature: 18–23°.

TABLE II.

Current quantity	$\alpha$ -naphthoquinone	$\alpha$ -naphthoquinone	Current yield of $\alpha$ -naphthoquinone	Material yield of $\alpha$ -naphthoquinone
		Current quantity		
amp. hr.	gr.	gr./amp. hr.	%	%
0.8	0.3859	0.4831	32.73	34.92
1.6	0.4490	0.2806	19.04	40.63
3.2	0.5169	0.1615	10.95	46.79
4.8	0.5904	0.1230	8.34	53.43
6.4	0.6591	0.1029	6.98	59.65
8.0	0.6110	0.0763	5.18	55.29

## 3. Influence of current density.

Anode solution : 1.0 gr.  $\alpha$ -naphthylamine  
 50 c.c. acetone  
 100 c.c.  $H_2SO_4$  (20%)

Anode : Lead peroxide (80 sq. cm.)

Cathode solution :  $H_2SO_4$  (20%)

Cathode : Lead

Current quantity : 1.6 ampère hours

Temperature : 18–23°.

TABLE III.

Current density	Voltage	$\alpha$ -naphthoquinone	Current yield of $\alpha$ -naphthoquinone	Material yield of $\alpha$ -naphthoquinone
amp./100 cm <sup>2</sup> .	volt	gr.	%	%
3	3.4–3.6	0.3355	14.22	30.36
2	3.2–3.3	0.4490	19.04	40.63
1	2.8–2.9	0.5643	23.97	51.07
0.5	2.5–2.7	0.5027	21.31	45.49

## 4. Influence of temperature.

Anode solution : 1.0 gr.  $\alpha$ -naphthylamine  
 50 c.c. acetone  
 100 c.c.  $H_2SO_4$  (20%)

Anode : Lead peroxide (80.0 sq. cm.)

Cathode solution :  $H_2SO_4$  (20%)

Current strength : 0.8 ampère

Current quantity : 1.6 ampère hours.

TABLE IV.

Temperature	Voltage	$\alpha$ -naphthoquinone	Current yield of $\alpha$ -naphthoquinone	Material yield of $\alpha$ -naphthoquinone
$^{\circ}\text{C.}$	volt	gr.	%	%
18—23	2.8—2.9	0.5643	23.97	51.07
40—50	3.1—3.3	0.3264	13.84	29.54

5. Influence of the concentration of sulphuric acid.

Anode solution : 1.0 gr.  $\alpha$ -naphthylamine

50 c.c. acetone

100 c.c.  $\text{H}_2\text{SO}_4$

Anode : Lead peroxide (80.0 sq. cm.)

Cathode solution :  $\text{H}_2\text{SO}_4$  (the same concentration as in the anode solution)

Cathode : Lead

Current strength : 0.8 ampère

Current quantity : 1.6 ampère hours

Temperature : 18—23 $^{\circ}$

TABLE V.

Concentration of sulphuric acid	Voltage	$\alpha$ -naphthoquinone	Current yield of $\alpha$ -naphthoquinone	Material yield of $\alpha$ -naphthoquinone
%	volt	gr.	%	%
10	2.7—2.8	0.5918	25.09	53.56
20	2.8—2.9	0.5643	23.97	51.07
30	3.1—3.2	0.5040	21.37	45.61
40	3.3—3.5	0.3892	18.79	35.22

6. Influence of the oxygen carrier.

Anode solution : 1.0 gr.  $\alpha$ -naphthylamine

50 c.c. acetone

100 c.c.  $\text{H}_2\text{SO}_4$  (10%)

0.5 gr. oxygen carrier

Anode : Lead peroxide (80.0 sq. cm.)

Cathode solution :  $\text{H}_2\text{SO}_4$  (10%)

Cathode : Lead  
 Current strength : 0.8 ampère  
 Current quantity : 0.8 ampère hour  
 Temperature : 18–23°

TABLE VI.

Oxygen carrier	Voltage	$\alpha$ -naphtho-quinone	Current yield of $\alpha$ -naphtho-quinone	Material yield of $\alpha$ -naphtho-quinone
	volt	gr.	%	%
Chrome alum	2.6–2.7	0.5614	43.31	50.85
Potassium chromate	2.4–2.6	0.6828	57.55	61.84
Potassium ferrocyanide	2.6–2.8	0.5193	45.77	47.02
Ferric sulphate	2.8–2.9	0.5263	44.36	47.67
Potassium chlorate	2.7–2.9	0.5900	49.73	53.44

## (c) OXIDATION OF A VIOLET COLOURING MATTER.

0.2 gram of a violet colouring matter was dissolved in a mixture of 50 c.c. of acetone and 20 c.c. of 10% sulphuric acid. A perforated lead plate coated with lead peroxide, about 40 sq. cm. served as the anode, and electrolysis was continued for 4 hours with a current of 0.4 ampère.

After electrolysis was over the anode liquid was extracted with ether. The ethereal extract was then evaporated, and the residue was subjected to steam distillation. The distillation product (about 0.108 gram) was identified as  $\alpha$ -naphthoquinone by the colour reactions. It was recrystallized from petroleum ether and was found to melt at 125°. By comparing with a pure specimen, it was confirmed to be  $\alpha$ -naphthoquinone. Phthalic acid was detected in the residue of the steam distillation.

## (d) OXIDATION OF 1-4-AMIDONAPHTHOL.

One gram of 1-4-amidonaphthol was dissolved in a mixture of 50 c.c. of acetone and 100 c.c. of 10% sulphuric acid. A perforated lead plate coated with lead peroxide, about 80.0 sq. cm. served as the anode, and electrolysis was continued for 1.5 hours with a current of 1.0 ampère.

After electrolysis the anode liquid was treated in an analogous



manner as in the previous experiments, the substance identified as  $\alpha$ -naphthoquinone by the colour reactions was isolated. On recrystallizing it from petroleum ether, 0.463 gram of the quinone melting at  $125^\circ$  was obtained.

$\alpha$ -Naphthoquinone isolated as above was analyzed with the following results:

0.1764 gr. substance gave 0.4888 gr.  $\text{CO}_2$  and 0.0639 gr.  $\text{H}_2\text{O}$ .

	Found	Cal. ( $\text{C}_{10}\text{H}_6\text{O}_2$ )
Carbon	75.57	75.93
Hydrogen	4.02	3.83

(2) ELECTROLYTIC OXIDATION OF AR-TETRAHYDRO- $\alpha$ -NAPHTHYLAMINE.

ar-Tetrahydro- $\alpha$ -naphthylamine sulphate used in my experiments prepared by Eug. Bamberger and F. Lengfeld's<sup>1</sup> method.

0.6397 gr. of the air-dried substance gave 0.0168 gr. water on sulphuric acid.

	Found	Cal. ( $\text{C}_{10}\text{H}_{11}\text{NH}_2$ ) <sub>2</sub> $\text{H}_2\text{SO}_4 + \frac{1}{2}\text{H}_2\text{O}$
$\text{H}_2\text{O}$	2.62	2.24

0.1405 gr. of the anhydrous substance gave 0.0826 gr.  $\text{BaSO}_4$ .

	Found	Cal. ( $\text{C}_{10}\text{H}_{11}\text{NH}_2$ ) <sub>2</sub> $\text{H}_2\text{SO}_4$
$\text{H}_2\text{SO}_4$	24.68	25.01

(a) PRELIMINARY EXPERIMENT.

I. The anode liquid, consisting of 100 c.c. of sulphuric acid (20%), 50 c.c. of acetone and 1.0 gram of ar-tetrahydro- $\alpha$ -naphthylamine sulphate, was introduced into a beaker. A porous cell was placed in it as the cathode compartment and sulphuric acid (20%) was poured into the beaker as the cathode liquid. As the anode a perforated lead plate coated with lead-peroxide, about  $10.0 \times 8.0$  cm. was used. The bath was cooled with running water to keep the temperature of it always at about  $20^\circ$ . Electrolysis was continued for nearly one hour with a current of 1.6 ampère.

<sup>1</sup> Ber. D. chem. Ges., 23, 1131 (1890).

On treating the anode solution in the usual way yellow needle crystals, melting at  $55.5^{\circ}$ , were obtained.

The yellow needle crystals were analyzed with the following results:

1. 0.1483 gr. substance gave 0.3993 gr.  $\text{CO}_2$  and 0.0914 gr.  $\text{H}_2\text{O}$ .
2. 0.1326 gr. substance gave 0.3585 gr.  $\text{CO}_2$  and 0.0775 gr.  $\text{H}_2\text{O}$ .

	1.	2.	Cal. ( $\text{C}_{10}\text{H}_{10}\text{O}_2$ )
Carbon	73.43	73.73	74.07
Hydrogen	6.84	6.54	6.17

From the result of this analysis there is no doubt that the yellow needle crystalline substance above obtained is ar-tetrahydro- $\alpha$ -naphthoquinone. By comparing it with a specimen prepared by Bamberger and Lengfeld's<sup>1</sup> method this was confirmed. A dark violet substance was obtained as the by-product but it was not further examined.

2. In the second experiment electrolysis was continued for nearly 3 hours with a current of 1.6 ampère. The yellow crystals, identified as ar-tetrahydro- $\alpha$ -naphthoquinone by a direct comparison with a pure specimen, were produced on distilling the anode solution with steam. The distillation residue was extracted with ether. The ethereal liquid was shaken up several times with a saturated sodium carbonate solution so as to dissolve any acid produced. The sodium carbonate solution was then neutralised with dilute sulphuric acid and again extracted with ether. After drying with anhydrous sodium sulphate, the ethereal extract was evaporated to a small volume. After standing it for a few days in the vacuum desiccator, a very small quantity of colourless needles melting at  $149-151^{\circ}$  was found to crystallize out.

(b) QUANTITATIVE INVESTIGATION.

In order to study the above oxidation reaction quantitatively the following experiments were carried out.

1. Influence of the anode material.

Anode solution: 1.0 sulphate

50 c.c. acetone

100 c.c.  $\text{H}_2\text{SO}_4$  (20%)

Cathode solution:  $\text{H}_2\text{SO}_4$  (20%)

Temperature:  $18-23^{\circ}$ .

<sup>1</sup> Loc. cit.

TABLE VII.

Anode		Cathode	Current strength	Voltage	Current quantity	ar-tetrahydro- $\alpha$ -naphthoquinone	Yield
Material	Surface area						
Platinum	sq. cm. 40.0	Spiral platinum	amp. 0.8	volt 3.1-3.2	amp. hr. 1.6	gr. 0.0081	% 2.18
Lead peroxide	80.0	Lead	0.8	2.7-2.8	1.6	0.1833	50.01
Graphite	45.0	Spiral platinum	0.9	2.5-2.7	1.8	very little	—

2. Influence of current quantity.

Anode solution : 1.0 gr. sulphate

50 c.c. acetone

100 c.c.  $H_2SO_4$  (20%)

Anode : Lead peroxide (80.0 sq. cm.)

Cathode solution :  $H_2SO_4$  (20%)

Cathode : Lead

Current density : 0.02 ampère per 1 sq. cm.

Temperature : 18-23°.

TABLE VIII.

Current quantity	ar-tetrahydro- $\alpha$ -naphthoquinone	Quinone		Yield
			Current quantity	
amp. hr.	gr.		gr./amp. hr.	%
1.6	0.1083		0.0676	29.54
2.4	0.1532		0.0638	31.80
3.2	0.1944		0.0607	53.04
4.0	0.1872		0.0468	51.07
4.8	0.1380		0.0287	37.65

3. Influence of current density.

Anode solution : 1.0 gr. sulphate

50 c.c. acetone

100 c.c.  $H_2SO_4$  (20%)

Anode : Lead peroxide (80.0 sq. cm.)

Cathode solution :  $H_2SO_4$  (20%)

Cathode : Lead

Current quantity : 1.6 ampère

Temperature : 18-23°.

TABLE IX.

Current density	Voltage	ar-tetrahydro- $\alpha$ -naphthoquinone	Yield
amp./100 cm <sup>2</sup> .	volt	gr.	%
3	3.1—3.2	0.0780	21.28
2	2.8—2.9	0.1083	29.54
1	2.7—2.8	0.1591	43.41

## 4. Influence of temperature.

Anode solution : 1.0 gr. sulphate  
 50 c.c. acetone  
 100 c.c. H<sub>2</sub>SO<sub>4</sub> (20%)  
 Anode : Lead peroxide (80.0 sq. cm.)  
 Cathode solution : H<sub>2</sub>SO<sub>4</sub> (20%)  
 Cathode : Lead  
 Current strength : 0.8 ampère  
 Current quantity : 1.6 ampère hours.

TABLE X.

Temperature	Voltage	ar-tetrahydro- $\alpha$ -naphthoquinone	Yield
°C.	volt	gr.	%
7—10	2.6—2.7	0.1291	35.22
18—23	2.7—2.8	0.1591	43.41
49—50	3.0—3.1	0.0526	14.35

## 5. Influence of the concentration of sulphuric acid.

Anode solution : 1.0 gr. sulphate  
 50 c.c. acetone  
 100 c.c. H<sub>2</sub>SO<sub>4</sub>  
 Anode : Lead peroxide (80.0 sq. cm.)  
 Cathode solution : H<sub>2</sub>SO<sub>4</sub> (The same concentration as in the anode solution)  
 Cathode : Lead  
 Current strength : 0.8 ampère  
 Current quantity : 1.6 ampère hours  
 Temperature : 18—23°.

TABLE XI.

Concentration of sulphuric acid	Voltage	ar-tetrahydro- $\alpha$ -naphthoquinone	Yield
%	volt	gr.	%
10	2.6—2.8	0.1833	50.01
20	2.7—2.8	0.1591	43.41
30	3.0—3.1	0.1205	32.87
40	3.3—3.5	0.0829	22.61

6. Influence of the oxygen carrier.

Anode solution : 1.0 gr. sulphate  
 50 c.c. acetone  
 100 c.c. H<sub>2</sub>SO<sub>4</sub> (10%)  
 0.3 gr. oxygen carrier

Anode : Lead peroxide (80.0 sq. cm.)

Cathode solution : H<sub>2</sub>SO<sub>4</sub> (10%)

Cathode : Lead

Current strength : 0.8 ampère

Current quantity : 0.8 ampère hour

Temperature : 18—20.

TABLE XII.

Oxygen carrier	Voltage	ar-tetrahydro- $\alpha$ -naphthoquinone	Yield
	volt	gr.	%
Chrome alum	2.6—2.7	0.1026	27.99
Potassium chromate	2.5—2.7	0.1138	31.05
Potassium ferrocyanide	2.9—3.1	0.0993	27.09
Potassium chlorate	3.0—3.1	0.1294	35.30

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