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Specification No. 51189. Application No. 51189, dated 3rd February 1954. Complete Specification left on 18th February 1954. (Application accepted 18th February 1955.)

PROVISIONAL SPECIFICATION.

PREPARATION OF CALCIUM GLUCONATE BY THE ELECTROLYTIC OXIDATION OF GLUCOSE.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1960).

*The following specification describes the nature of this invention.*

THIS IS AN INVENTION BY BIMAN BHARI DEY, HANDADY VENKATAKRISHNA UDUPA AND VAIRELIL SARADA MENON, ALL OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAKUDI, S. RLY., INDIA, ALL INDIAN CITIZENS.

This invention relates to a process for the preparation of calcium gluconate by the electrolytic oxidation of glucose.

Fink and Summers (Trans. Electrochem. Soc. 74, 625 (1938)) oxidised an aqueous solution of glucose containing 2 per cent. sodium bromide, at a graphite anode (current density=1 to 2 amps./dm<sup>2</sup>, Temperature=40° C.). They found that they could obtain a 95 per cent. yield of calcium gluconate, by passing 10 per cent. excess of the theoretical current required for the purpose. Their loss of bromine was 25 per cent. or more, and since the loss had to be made up in successive experiments, the cost of production depended materially on this replacement of bromide. Fink and Summers claimed to have minimized the loss of bromine to about 3 per cent. by changing the direction of the rectifier A.C. every fifteen minutes.

The present invention consists in the use of a rotating graphite anode for the purpose of oxidation of glucose. By the use of this technique we have been able to achieve the following results:

(a) Much higher current densities of the order of 10 amps./dm<sup>2</sup> could be employed without the efficiency of oxidation suffering in the least.

(b) High efficiency of oxidation (96 to 98 per cent.) is attained even with the passage of the theoretical amount of current. (Fink and Summers found 10 per cent. excess of current to be necessary).

(c) The use of high current density (5 to 10 times that used by Fink and Summers) reduces the period of oxidation as well as the size of the cell-unit for the production of the same amount of calcium gluconate. (These factors should be considered to be of great importance from the point of view of adoption of the process on an industrial scale).

(d) The arrangement devised by Fink and Summers, called by them an "Alternator", for avoiding the loss of bromine, was dispensed with by using the rotating anode whereby the bromine loss was reduced to the same amount as that obtained by Fink and Summers.

Experiments have been carried out using the stationary anode and putting in an auxiliary stirrer, (as done by previous authors) as well as by rotating the anode itself without a stirrer. The results obtained show that at current densities of 8-10 amps./dm<sup>2</sup> the oxidation efficiency falls down to as low as 60 per cent. when a stationary anode is employed, whereas at a rotating anode the efficiency is as high as 98 per cent. while the bromine loss is maintained as low as 2 to 4 per cent.

The rotating anode need not necessarily be cylindrical. It could also be of the disc-type as shown in the diagram with greater or less number of discs, either to have large or small area of the anode.

The electrolytic oxidation of glucose is carried out under the following conditions, namely, the use of (a) a 2 per cent. alkali bromide solution as electrolyte, (b) a mole of glucose per litre in solution, (c) iron or graphite cathodes, (d) graphite anode, (e) no diaphragm, (f) a temperature of 35° C., and (g) a current density of 2 to 13 amps./dm<sup>2</sup>.

Along with 2 per cent. alkali bromide (KBr, NaBr), 2 per cent. alkali halide (NaCl, KCl) can be used to improve the conductivity of the bath. Efficiency of oxidation, however, was only 92.7 per cent. when 8.4 amps./dm<sup>2</sup> was used.

In the preparation of calcium gluconate by the addition of calcium carbonate into the electrolyte, up to one molar sugar solution can be used without precipitating calcium gluconate in the cell itself.

Temperature up to 45° C. is permissible. At higher temperatures bromine loss would be objectionable. At lower temperatures, although bromine loss is less, cooling costs become excessive. In our experiments, 35° C. was used.

A very wide range of current density (2 to 13 amps./dm<sup>2</sup>) could be employed in this invention without either affecting the current efficiency of oxidation, or increasing the bromine loss to objectionable limits. Still higher current density can be tried but cell will have to be cooled to maintain the temperature at 35° C.

Bromine loss is reduced by the use of this new technique. At 7 amps./dm<sup>2</sup>, for example, bromine loss is 10.7

per cent. at a stationary anode whereas it is only 2.2 per cent. at a rotating anode.

The invention will now be described with reference to the accompanying drawings wherein Figure 1 and 2 represent the plan and elevation of the cylindrical graphite anode use in our investigation. "A" in Figure 2 represents a copper rod threaded at the lower end so as to fit into a graphite rod "C", the top portion "B" of which has been slightly reduced in diameter. Only the portion "C" is immersed during the reaction.

Figure 3 and Figure 4 similarly represent the plan and elevation of the disc type graphite anode. A' represents copper rod in Figure 4 which is threaded into the graphite rod B' graphite discs, D, are mounted on the graphite rod B' and are held in place by means of graphic spacers which are threaded on to the lower part of the graphite rod B'. The length of spacers can be increased to give proper approach of the electrolyte during oxidation. Similarly more discs or less discs could be included depending on the anode area required for oxidation purpose.

The disc type anode, Figure 3 and Figure 4, could also be made from a single graphite rod of required diameter, by careful machining of the same.

EXAMPLES.

1(a): 50 gms., of glucose (on analysis 43 gms.) dissolved in 450 cc., of 2 per cent. sodium bromide was electrolysed in a 600 cc., beaker at a rotating cylindrical graphite anode (R.P.M., about 3,500/) and graphite cathode for an hour and ten minutes at an anode current density of 8.4 amps./dm<sup>2</sup> (9.5 amps.-current strength) and 35° C. The calculated amount of calcium carbonate was added in the beginning itself. Sugar analysis by Walker-Munson method indicated 99.45 per cent. efficiency of oxidation. Bromide estimation by Volkard's method showed a loss of only 1.79 per cent. of bromine. 44.8 gms., of calcium gluconate was separated by the addition of rectified spirit into the electrolyte after filtering off the excess calcium carbonate.

(b): A similar experiment at a stationary anode employing an auxiliary stirrer gave only 68.3 per cent. efficiency of oxidation.

Bromine loss was 2.89 per cent. The loss would naturally be still greater if the experiment was carried on till the efficiency of oxidation increased to that given above.

II(a): At a rotating anode using a current density of 7.08 amps./dm<sup>2</sup> (current strength=8 amps.) and keeping all other conditions same as in experiment 1, the current efficiency was 97.1 per cent. and bromine loss was 2.2 per cent.

(b) At a stationary anode the efficiency of oxidation and bromine loss under the same conditions were 92.1 per cent. and 10.7 per cent. respectively.

III. 77.8 gms., of glucose when oxidized with 11.5 amps., current strength (10.2 amps./dm<sup>2</sup>) under same conditions as in I, gave 67.1 gms., of calcium gluconate on cooling the electrolyte. Efficiency of oxidation was 97.7 per cent. Nearly 70 per cent. of calcium gluconate separated on cooling. The filtrate can be fortified with more alkali bromide and used again for oxidation of a fresh amount of glucose.

The following are among the advantages of the present invention:

(1) Very high current densities can be used without lowering efficiency of oxidation in any way. For oxidation of a given amount of sugar, period of oxidation is, therefore, considerably shortened using a rotating anode instead of a stationary anode.

(2) Bromine loss is very much reduced necessitating the use of only very small amounts of bromide for replacement.

(3) When rotating anode is employed in commercial practice, for the same current the cell-unit will be more compact and, therefore, of high capacity, resulting in a considerable saving in floor-space.

R. BHASKAR PAI.

Patents Officer,

Council of Scientific & Industrial Research.

Dated this 2nd day of February 1954.

Price: TWO RUPEES.

## COMPLETE SPECIFICATION.

## PREPARATION OF CALCIUM GLUCONATE BY THE ELECTROLYTIC OXIDATION OF GLUCOSE.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI-1, INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1960).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

THIS IS AN INVENTION BY BIMAN BIHARI DEY, HANDADY VENKATAKRISHNA UDUPA AND VAIRELIL SARADA MENON, ALL OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAKUDI, S. RIV., INDIA, ALL INDIAN CITIZENS.

This invention relates to a process for the preparation of calcium gluconate by the electrolytic oxidation of glucose.

Fink and Summers (Trans. Electrochem Soc. 74, 625 (1938)) oxidised an aqueous solution of glucose containing 2 per cent. sodium bromide, at a graphite anode (current density = 1 to 2 amps./dm<sup>2</sup>, Temperature = 40° C.). They found that they could obtain a 95 per cent. yield of calcium gluconate, by passing 10 per cent. excess of the theoretical current required for the purpose. Their loss of bromine was 25 per cent. or more, and since the loss had to be made up in successive experiments, the cost of production depended materially on this replacement of bromide. Fink and Summers claimed to have minimized the loss of bromine to about 3 per cent. by changing the direction of the rectified A.C. every fifteen minutes.

The present invention consists in the electrolytic oxidation of glucose to gluconic acid in the presence of alkali bromide as electrolyte (and the subsequent reaction of gluconic acid with the added calcium carbonate or lime to give calcium gluconate) and is characterised in that the cell in which the electrolytic oxidation is carried out, is provided with a rotating graphite anode. (When lime is used, it is added in stages to maintain very nearly neutral condition of the electrolyte).

By the use of a rotating graphite anode for the purpose of oxidation of glucose we have been able to achieve the following results:

- (a) Much higher current densities of the order of 20 amps./dm<sup>2</sup> could be employed without the efficiency of oxidation suffering in the least.
- (b) High efficiency of oxidation (96 to 98 per cent.) is attained even with the passage of the theoretical amount of current. (Fink and Summers found 10 per cent. excess of current to be necessary).
- (c) The use of high current density (6 to 10 times that used by Fink & Summers) reduces the period of oxidation as well as the size of the cell-unit for the production of the same amount of calcium gluconate. (These factors should be considered to be of great importance from the point of view of adoption of the process on an industrial scale).
- (d) The arrangement devised by Fink and Summers, called by them an "Alternator", for avoiding the loss of bromine, was dispensed with by using the rotating anode whereby the bromine loss was reduced to the same amount as that obtained by Fink and Summers.

Experiments have been carried out using the stationary anode and putting in an auxiliary stirrer, (as done by previous authors) as well as by rotating the anode itself without a stirrer. The results obtained show that at current densities of 15-18 amps./dm<sup>2</sup> the oxidation efficiency falls down to as low as 60 per cent. when a stationary anode is employed, whereas at a rotating anode the efficiency is as high as 98 per cent. while the bromine loss is maintained as low as 2 to 4 per cent.

The rotating anode need not necessarily be cylindrical. It could also be of the disc-type as shown in the diagram with greater or less number of discs, either to have large or small area of the anode.

The electrolytic oxidation of glucose is carried out under the following conditions, namely, the use of (a) a 2 per cent. alkali bromide solution as electrolyte, (b) a mole of glucose per litre in solution, (c) iron or graphite cathodes, (d) graphite anode, (e) no diaphragm, (f) a temperature of 35° C., and (g) a current density of 2 to 28 amps./dm<sup>2</sup>, and (h) amount of calcium carbonate or lime required to neutralize gluconic acid.

Along with 2 per cent. alkali bromide (KBr, NaBr), 2 per cent. alkali halide (NaCl, KCl) can be used to improve the conductivity of the bath. Efficiency of oxidation however, was only 92.7 per cent. when 17.8 amps./dm<sup>2</sup> was used.

In the preparation of calcium gluconate by the addition of calcium carbonate into the electrolyte, up to one molar sugar solution can be used without precipitating calcium gluconate in the cell itself.

Temperature up to 45° C. is permissible. At higher temperatures bromine loss would be objectionable. At lower temperatures, although bromine loss is less, cooling costs become excessive. In our experiments, 35° C. was used.

A very wide range of current density (2 to 28 amps./dm<sup>2</sup>) could be employed in this invention without either affecting the current efficiency of oxidation, or increasing the bromine loss to objectionable limits. Still higher current density can be tried but cell will have to be cooled to maintain the temperature at 35° C.

Bromine loss is reduced by the use of this new technique. At 17 amps./dm<sup>2</sup>, for example, bromine loss is

10.7 per cent. at a stationary anode whereas it is only 2.2 per cent. at a rotating anode.

The invention will now be described with reference to the drawings accompanying the provisional specification wherein Figure 1 and 2 represent the plan and elevation of the cylindrical graphite anode used in our investigation. "A" in Figure 2 represents a copper rod (about 24 cm. long and 0.6 cm. diameter) threaded at the lower end so as to fit into a graphite rod "4" (8 cm. long and 2 cm. diameter), the top portion "B" (4 cm. long) of which has been slightly reduced in diameter (1.5 cm. diameter). Only the portion "C" is immersed during the reaction (total area immersed: 0.534 dm<sup>2</sup>).

Figure 3 and Figure 4 similarly represent the plan and elevation of the disc type graphite anode. A' represents copper rod (about 13 cm. long and 0.6 cm. in diameter) in Figure 4, which is threaded into the graphite rod B' (13 cm. long and 1.25 cm. in diameter). Graphite discs, D (5 cm. in diameter and 0.5 cm. thick), are mounted on the graphite rod B', and are held in place by means of graphite spacers (1 cm. long) which are threaded on to the lower part of the graphite rod B'. The length of spacers can be increased to give proper approach of the electrolyte during oxidation. Similarly more discs or less discs could be included depending on the anode area required for oxidation purpose, total area available for oxidation being 2.2 dm<sup>2</sup>.

The disc type anode, Figure 3 and Figure 4, could also be made from a single graphite rod of required diameter, by careful machining of the same.

## EXAMPLES.

I (a): 50 gms., of glucose (on analysis 43 gms.) dissolved in 450 cc., of 2 per cent. sodium bromide was electrolysed in a 600 cc. beaker at a rotating cylindrical graphite anode (R.P.M., about 3,500/!) and graphite cathode for an hour and ten minutes at an anode current density of 8.4 amps./dm<sup>2</sup> (9.5 amps. current strength) and 35° C. The calculated amount of calcium carbonate was added in the beginning itself. Sugar analysis by Walker-Munsen method indicated 99.45 per cent. efficiency of oxidation. Bromide estimation by Volhard's method showed a loss of only 1.79 per cent. of bromine. 44.8 gms., of calcium gluconate was separated by the addition of rectified spirit into the electrolyte after filtering off the excess calcium carbonate.

(b): A similar experiment at a stationary anode employing an auxiliary stirrer gave only 68.5 per cent. efficiency of oxidation.

Bromine loss was 2.89 per cent. The loss would naturally be still greater if the experiment was carried on till the efficiency of oxidation increased to that given above.

II (a): At a rotating anode using a current density of 15 amps./dm<sup>2</sup> (current strength = 8 amps.) and keeping all other conditions same as in experiment I, the current efficiency was 97.1 per cent. and bromine loss was 2.2 per cent.

(b) At a stationary anode the efficiency of oxidation and bromine loss under the same conditions were 92.1 per cent. and 10.7 per cent. respectively.

III. 77.8 gms., of glucose when oxidized with 11.5 amps. current strength (CD. 21.5 amps./dm<sup>2</sup>) under same conditions as in I, gave 67.1 gms., of calcium gluconate on cooling the electrolyte. Efficiency of oxidation was 97.7 per cent. Nearly 70 per cent. of calcium gluconate separated on cooling. The filtrate can be fortified with more alkali bromide and used again for oxidation of a fresh amount of glucose.

The following are among the advantages of the present invention:

(1) Very high current densities can be used without lowering efficiency of oxidation in any way. For oxidation of a given amount of sugar, period of oxidation is, therefore, considerably shortened using a rotating anode instead of a stationary anode.

(2) Bromine loss is very much reduced necessitating the use of only very small amounts of bromide for replacement.

(3) When rotating anode is employed in commercial practice, for the same current, the cell-unit will be more compact and, therefore, of high capacity, resulting in a considerable saving in floor-space.

## We claim:

1. A process for the preparation of calcium gluconate which consists in the electrolytic oxidation of glucose to gluconic acid in the presence of alkali bromide as electrolyte (and the subsequent reaction of gluconic acid with the added calcium carbonate or lime to give calcium gluconate) which is characterised in that the cell in which electrolytic oxidation of glucose is carried out is provided with a rotating graphite anode.

2. A process as claimed in Claim 1 wherein the cell is provided with a rotating cylindrical anode.
3. A process as claimed in Claim 1 wherein the cell is provided with a disc-type rotating anode of which the number of discs can be increased or reduced to have a comparatively larger or smaller area of the anode.
4. A process as claimed in any of the preceding claims wherein the electrolytic oxidation of glucose is conducted under the following conditions, namely, the use of (a) a 2 per cent. alkali bromide solution as electrolyte, (b) a mole of glucose per litre in solution, (c) iron or graphite cathodes, (d) graphite anode, (e) no diaphragm, (f) a temperature of 35° C., and (g) a current density of 2 to 28 amps./dm<sup>2</sup>, and (h) amount of calcium carbonate or lime require to neutralize gluconic acid.
5. A process as claimed in Claim 4 wherein along with 2 per cent. alkali bromide (KBr, NaBr), 2 per cent. alkali halide (NaCl, KCl) is used.
6. A process as claimed in any of the preceding claims wherein calcium gluconate is prepared by the addition of calcium carbonate in the electrolytic, up to one molar sugar solution being used without precipitating calcium gluconate in the cell itself.
7. A process as claimed in any of the preceding claims wherein the oxidation is conducted at a temperature up to 45° C.
8. A process as claimed in Claim 7 wherein the temperature is maintained at 35° C.
9. A process as claimed in any of the preceding claims wherein the current density is 2 to 28 amp./dm<sup>2</sup>.
10. A process as claimed in Claim 9 wherein a higher current density is employed but the cell is cooled to maintain the temperature at 35° C.
11. A process for the preparation of calcium gluconate by the electrolytic oxidation of glucose substantially as described in the examples.
12. Calcium gluconate obtained according to a process substantially as hereinbefore described.

R. BHASKAR PAI,

Patents Officer,

Council of Scientific & Industrial Research,

Dated this 9th day of February 1954.

COUNCIL OF SCIENTIFIC &  
INDUSTRIAL RESEARCH  
NO. 51189

TWO SHEETS  
SHEET 1

PROVISIONAL  
SPECIFICATION

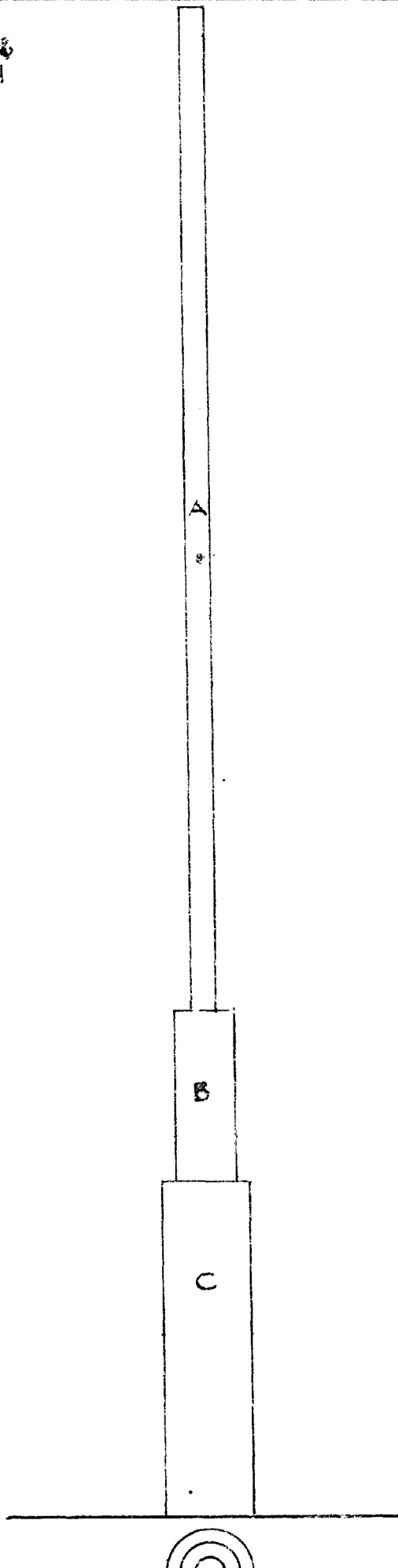


FIG. 2

PROVISIONAL  
SPECIFICATION

FIG: 4

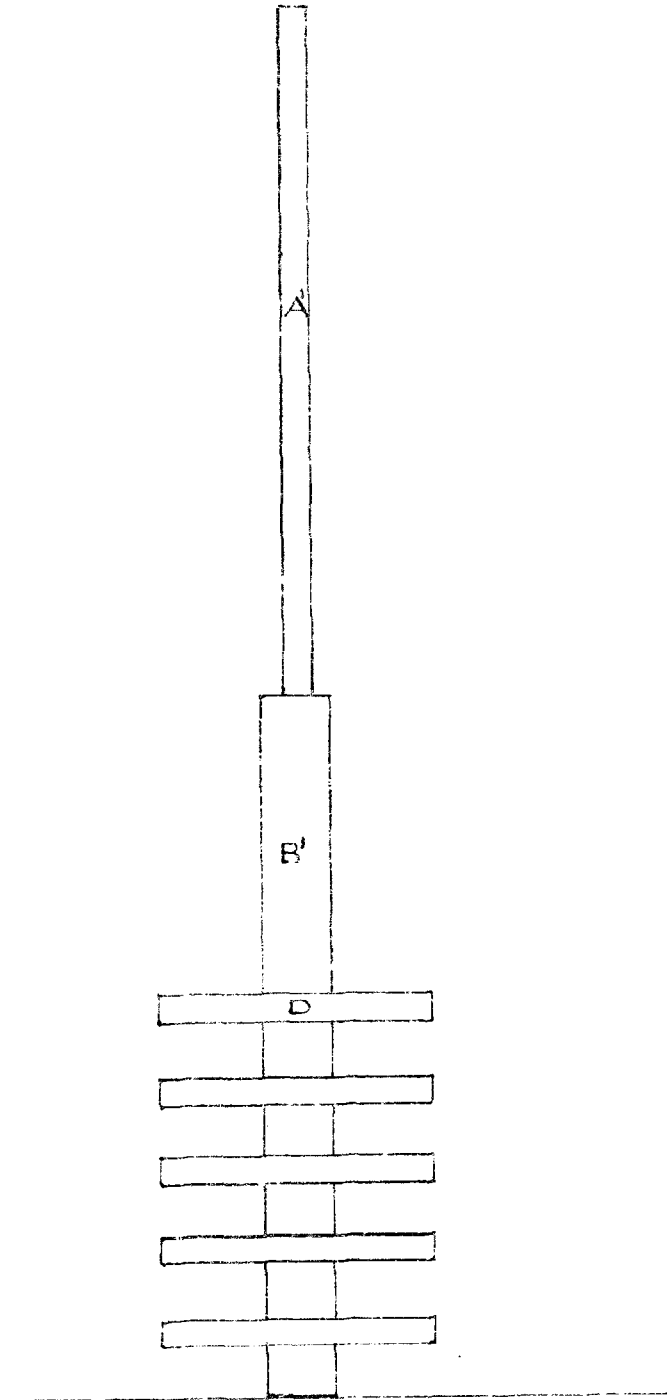


FIG: 3

