

GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 79075, Application No. 79075, dated 28th October 1961. Complete specification left on 25th July 1962. (Application accepted 16th April 1963.)

IMPROVEMENTS IN OR RELATING TO THE TWO STAGE ELECTROCHEMICAL PRODUCTION OF DIALDEHYDE STARCH.

PROVISIONAL SPECIFICATION.

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 1860).

The following specification describes the nature of this invention.

This is an invention by HANDADY VENKATAKRISHNA UDUPA, MYSORE SESHAIYER VENKATACHALAPATHY and RENGANATHAN RAMASWAMY, all of the Central Electrochemical Research Institute, Karaikudi, Madras, India, all Indian citizens.

Periodic acid was first introduced as a reagent for the oxidation of 1,2-glycols by Malaprade in 1928 but its application for industrial purposes was limited by its high cost. The electrolytic preparation of dialdehyde starch was studied later by C.L. Mehlretter using iodic acid in the electrolytic cell itself wherein the periodate was continuously regenerated *in situ*.

It has now been established by us that single step process gives very poor current efficiency for continuous processes and two-stage process is more economical for electro-organic oxidations in general using inorganic reagents. Recently, Pfeifer and his co-workers have developed such a two-stage process for the production of dialdehyde starch, employing periodic acid (periodate) prepared electrolytically from crude iodine. However, Pfeifer's process suffers from the following defects:

- 1) The proper choice of the diaphragm and the periodic replacement of the diaphragm.
- 2) The loss of iodate ion due to the influence of Electro-osmosis.
- 3) The neutralisation of the iodic acid with NaOH solution before reacting with starch.
- 4) The corrosion of anode during oxidation leading to the need for subsequent replacement of anodes.

The abovementioned difficulties and obstacles are easily avoided by the modifications and improvements now effected by us in the process by the technique of using suitably shaped nickel plated metal (iron or copper) cathodes covered by asbestos fibre only or any other suitable material and by using electrodeposited lead dioxide or lead dioxide electrodeposited over graphite or carbon (as in Indian Patent No. 66,195) as anodes or lead or suitable lead alloy as anodes. Hence the present process is superior to the process hitherto described in literature, since it not only minimises the anode corrosion when electrodeposited lead dioxide anode is employed but also eliminates the additional expenses incurred in maintaining a separate cathode chamber and then of neutralising the anolyte with sodium hydroxide solution from catholyte before reacting with starch.

By employing a closely fitting diaphragm on the cathode as described above only build up of hydroxyl ion concentration in the pores of the diaphragm occurs which readily mixes with the anolyte. Adverse potential gradient in the pores of the diaphragm is thus sufficient to prevent the reduction of iodate ion. Diaphragm used in this way is very effective and does not cause an excessive IR drop or polarization potential.

Pfeifer's process employs cornstarch as the raw material whereas we utilise indigenous tapioca starch as the raw material which is available in plenty in India. The process has also been tried for maize starch.

The process now developed consists in, first preparing a concentrated solution of iodic acid by electrolytic oxidation of iodine or sodium iodide, using either graphite or electrodeposited lead dioxide (over graphite or carbon substrates) as anodes and secondly oxidising the iodic acid to periodic acid at a lead dioxide anode (first stage). The periodic acid solution thus obtained was then reacted (second stage) with tapioca starch outside the cell to be oxidized to polymeric dialdehyde starch. After the reaction was complete, dialdehyde starch was removed from the electrolyte and washed thoroughly so that the spent electrolyte (containing iodic acid) was recycled through

the electrolyzers for the regeneration of periodic acid. The process is described in detail in the following paragraphs.

Oxidation of iodic to periodic acid:

Iodic acid was oxidized to periodic acid in an electrolytic cell fitted with lead dioxide anodes and nickel-plated iron cathodes covered with asbestos cloth or ropes. When lead dioxide formed over lead was used as anode, the anode loss was about 2 to 2.5 g for 100 amp-hr and 1.62 g for 1% silver-lead alloy, whereas the anode loss was about 0.2 to 0.3 g for 100 amp-hr by using lead dioxide electrodeposited on graphite as anode. The anodes and cathodes were mounted on a wooden support using a glass container as cell. Pre-electrolysis using the anode was found to be important before the commencement of electrolysis. The electrolyte was agitated occasionally by an air-blower device. The concentration of iodic acid was kept between 2.5 to 10 percent but a solution of 10% concentration could give the maximum current efficiency and yield. The temperature of oxidation could vary from 24-45°C. but a temperature of 35°C. was employed for most of the experiments. A current density of 2.5 amp/dm² to 5.0 amp/dm² could be employed. A current efficiency of 60% and an yield of 94% periodate was obtained by using a prepolarised lead dioxide formed over lead as anode and a pretransformed deposited lead dioxide anode (with graphite substrate) was found to give as good current efficiency as lead dioxide formed on lead itself. A quantitative conversion of iodic acid to periodic acid was obtained. After removing the suspended impurities, the periodic acid in the electrolyte was estimated and the solution pumped to the oxidation tank.

Oxidation of Tapioca starch by periodic acid:

Hard rubber buckets provided with glass cooling coils and air-blower device for agitation was used as oxidation tank. Oxidation could be carried out at 20°C. to 35°C. the duration of oxidation being reduced at higher temperatures. The mole ratio of periodic acid to tapioca starch was varied from 1.0 to 1.25 and a mole ratio of 1.10 was found quite suitable for the purpose. The pH of the oxidant could be varied in the range 1 to 3.5, but a pH of 2.0 to 2.5 was found to be optimum. Keeping the mole ratio of periodic acid to starch as mentioned above, the concentration of periodic acid could be varied from 2.5 to 10% but a 9% solution at a temperature of 35°C. was found to be advantageous. The required quantity of tapioca starch was added and agitated by blowing air into the reactor. After the reaction was over, the oxidised starch was allowed to settle for about 2 hours and the clear supernatant liquid was syphoned to the electrolyzer. The remaining slurry was filtered under suction or centrifuged and washed well with water. The filtrate was collected and returned to the electrolyzer for regeneration and the dialdehyde starch was dried in air. An overall current efficiency of 75% was obtained with a dialdehyde content of 82% in the product and an energy consumption of 5.1 kw-hr per kilogram of dialdehyde starch.

The presence of organic impurities in the spent electrolyte decreases the current efficiency for the regeneration of periodic acid. The spent purified electrolyte only is recirculated for regeneration of periodic acid.

EXAMPLES

(a) Iodine to iodic acid (Iodide to Iodate):

150 g of sodium iodide or 127 g of iodine along with

Price : TWO RUPEES.

40 g of sodium hydroxide was dissolved in 750 cc of distilled water containing 1.5 g of sodium or potassium chromate. When lead dioxide formed on lead was used as anode, 25 g of sodium sulphate was added to the above solution. Either lead dioxide on lead or electrodeposited lead dioxide over graphite could be employed as anode. Stainless steel was used as cathode. During the oxidation, the temperature was kept between 40-45°C. and the pH was in the range of 8-9.5. A current density of 7.5 amp/dm² (in the case of lead dioxide on graphite, 25 amp/dm²) was employed and after passing 85% of the theoretical current required (136 amp-hrs) the whole solution was cooled to the room temperature (30°C.) and the separated needle shaped crystals washed well with distilled water and dried. 97 g of sodium iodate crystallised out and 35 g was obtained in the mother liquor and thereby a conversion efficiency of 82% was obtained. The mother liquor was preserved for subsequent runs.

(b) *Iodic acid to Periodic acid (Iodate to Periodate):*

(i) 200 g of sodium iodate was dissolved in 2 l of distilled water containing 23 g of sulphuric acid. The pH of the electrolyte was 2.5 to 3.0 and the temperature was kept at 35-40°C. Lead dioxide was used as anode and nickel plated iron cathode covered by asbestos rope was used as cathodes. No catholyte was used. The anodic current density was 5 amp/dm². 180 g of periodic acid was obtained with a current efficiency of 50% for a 90% yield.

(ii) *Iodic acid to Periodic acid (use of Nylon diaphragm):* 20 g of sodium iodate was dissolved in 200 cc of distilled water containing 2 g of sulphuric acid. The pH of the electrolyte was 2.5-3.0 and the temperature was kept at 30-35°C. Lead dioxide was used as anode and stainless steel covered with nylon cloth was used as cathodes. No separate cathode chamber was used. The anodic current density was 5 amp/dm². 17.9 g of sodium periodate was obtained with a current efficiency of 38% for a 83% yield.

(iii) *Iodic acid to periodic acid (Use of nylon with asbestos diaphragm):* The conditions are the same as described in (ii). The cathodes were first covered with asbestos and then nylon cloth was tightly fitted over it. 18.4 g of sodium periodate was obtained with a current efficiency of 42% for 85% yield.

(c) *Oxidation of tapioca starch by periodic acid (Periodate):*

275 g of periodic acid diluted to 3 litres was cooled to 30°C. and the pH adjusted to 2.5. Then 275 g of tapioca starch (10% moisture) was added in portions with agitation. After the completion of the oxidation (4 hours), it was allowed to settle and the supernatant liquor was pumped to the electrolyser. During oxidation, periodic acid was converted to iodic acid. Then the sludge was centrifuged and washed well with distilled water. The dialdehyde starch was dried in air and powdered. 230 g of dialdehyde starch with a dialdehyde content of 82% was obtained. The wash water after concentration, was sent to the electrolyser for the regeneration of periodic acid and an overall current efficiency of 77% was obtained for dialdehyde starch formation. The experiments were continued with the same electrolyte and in the second, third and fourth runs, 252 g, 250 g, and 220 g of dialdehyde starch was obtained giving overall current efficiency of 75%, 74.8% and 65% respectively.

The following are the special features of the process:

(1) A process for the preparation of dialdehyde starch in two stages consisting of oxidising the tapioca starch or other starch materials with periodic acid obtained in the first stage by the electrolytic oxidation of iodic acid in a cell containing essentially a cathode closely wrapped with asbestos cloth or rope or any other suitable material and an anode of lead dioxide either formed on lead or lead alloys or electrodeposited to suitable sizes.

(2) A process as above in which iodic acid for the preparation of periodic acid is prepared by electrolytic oxidation of iodine using graphite or lead dioxide formed on lead or lead alloys or electrodeposited lead dioxide as anodes and using stainless steel as cathode.

(3) A process as in (1) wherein the iodic acid is oxidized to periodic acid using lead dioxide formed on lead or lead alloys or lead dioxide electrolytically deposited on graphite, carbon or any other suitable substrate or lead dioxide deposited to suitable sizes as anodes.

(4) A process as in (1) wherein stainless steel, iron, copper, nickel or nickel-plated metals wrapped with asbestos rope or cloth as cathodes.

(5) A process as in (1) wherein a current density of 1 to 10 amp/dm² but preferably 5 amp/dm² and temperature range of 30-45°C., but preferably 35 to 40°C. and a pH of 1 to 4 but preferably 2.5 to 3 are employed so as to obtain quantitative conversion of iodic acid to periodic acid in the first stage.

(6) A process as in (1) wherein the solution of periodic acid obtained in the first stage from the electrolytic cell is allowed in the second stage to react with either tapioca starch or any other starch material by agitation in a separate reactor.

(7) A process as in (6) wherein the oxidation of starch is carried out at a temperature of 20 to 35°C. but preferably at 25°C.

(8) A process as above wherein a mole ratio of starch to periodic acid of 1 to 1.5 is used for the oxidation reaction.

(9) A process as in (6) wherein the pH of the periodic acid during oxidation of starch is kept within the range of 1 to 3.5 but preferably at 2.5.

(10) A process as above wherein the corresponding dialdehyde starch formed is recovered by centrifuging or filtration under suction and washed well with water to free the product from electrolyte.

(11) A process as referred to above wherein the process of oxidation of iodine to periodic acid in the first stage, oxidation of tapioca starch or any other starch to dialdehyde starch in the second stage and the regeneration of periodic acid from iodic acid followed by subsequent oxidation of further amount of starch is made cyclic on a practical scale.

(12) Production of dialdehyde starch by oxidation of either tapioca starch or any other starch by periodic acid prepared according to the process as hereinbefore described.

R. BHASKAR PAI,

Patents Officer,

Council of Scientific and Industrial Research.

Dated 12th day of October, 1961.

COMPLETE SPECIFICATION.

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 HANDADY VENKATAKRISHNA UDUPA, MYSORE SHESHAIYER VENKATACHALAPATHY and RENGANATHAN RAMASWAMY, all of the Central Electrochemical Research Institute, all Indian subjects.

This invention relates to improvements in or relating to the two stage electrochemical production of dialdehyde starch from starch.

Periodic acid was first introduced as a reagent for the oxidation of 1,2-glycols by Malaprade in 1928 but its appli-

cation for industrial purposes was limited by its high cost. The electrolytic preparation of dialdehyde starch was studied later by C.L. Mehlretter using iodic acid in the electrolytic cell itself wherein the periodate was continuously regenerated *in situ*.

It has now been established by us that single step process gives very poor current efficiency for continuous processes and two-stage process is more economical for electro-organic oxidations in general using inorganic reagents. Recently, Pfeifer and his co-workers have developed such a two-stage process for the production of dialdehyde starch, employing periodic acid (periodate) prepared electrolytically from crude iodine. However, Pfeifer's process suffers from the following defects:

- 1) The proper choice of the diaphragm and the periodic replacement of the diaphragm.
- 2) The loss of iodate ion due to the influence of electro-osmosis.
- 3) The neutralisation of the iodic acid with NaOH solution before reacting with starch.
- 4) The corrosion of anode during oxidation leading to the need for subsequent replacement of anodes.

The abovementioned difficulties and obstacles are easily avoided by the modifications and improvements now effected by us.

According to the present invention, the process for the electrochemical production of dialdehyde starch by (i) the electrolytic oxidation of iodic acid to periodic acid (first stage), followed by (ii) oxidation of tapioca starch or like starch material by periodic acid (second stage) is characterised in that the electrolytic oxidation of iodic acid is carried out in a cell in which lead or 1% lead-silver alloy on which lead dioxide has been formed or electrodeposited lead dioxide having graphite or carbon substrate or without a substrate, are used as anodes, and cathodes closely wrapped with asbestos cloth or rope or nylon cloth are used.

The iodic acid for the preparation of periodic acid is prepared by electrolytic oxidation of iodine using lead dioxide formed on lead or lead alloys or electrodeposited lead dioxide as anodes and using stainless steel as cathode. Alternatively, iodic acid is prepared by electrolytic oxidation of iodine using graphite anode and using stainless steel as cathode.

Thus iodic acid is oxidised to periodic acid using lead dioxide formed on lead or lead alloy or lead dioxide electrolytically deposited on graphite or carbon substrates or deposited lead dioxide from which the substrates have been removed, as anodes; and stainless steel, iron, nickel or nickel-plated copper, nickel-plated iron or nickel-plated brass wrapped with asbestos cloth or rope are used as cathodes.

A current density of 1 to 10 amp/sq.dm. but preferably 5 amp/sq.dm. and a temperature range of 30-45°C. but preferably 35-40°C. and a pH of 1 to 4 but preferably 2.5 to 3 are employed to obtain quantitative conversion of iodic acid to periodic acid in the first stage.

The solution of periodic acid obtained in the first stage from the electrolytic cell is allowed in the second stage to react with either tapioca starch or any other like starch material by agitation in a separate reactor. The oxidation of starch is carried out at a temperature of 20 to 35°C. but preferably at 25°C. A mole ratio of starch to periodic acid of 1 to 1.5 is used for the oxidation reaction. The pH of the periodic acid during oxidation of starch is kept within the range of 1 to 3.5 but preferably at 2.5. Dialdehyde starch formed is recovered by centrifuging or filtration under suction and washed well with water to free dialdehyde starch from electrolyte.

The process of oxidation of iodine to periodic acid in the first stage, oxidation of tapioca starch or any other like starch material to dialdehyde starch in the second stage and the regeneration of periodic acid from iodic acid followed by subsequent oxidation of further amount of starch can be made cyclic.

The present process is superior to the processes hitherto described in literature, since it not only minimises the anode corrosion when electrodeposited lead dioxide anode is employed but also eliminates the additional expenses incurred in maintaining a separate cathode chamber and then of neutralising the anolyte with sodium hydroxide solution from catholyte before reacting with starch.

By employing a closely fitting asbestos fibre or cloth or nylon cloth as diaphragm on the cathode as described above only build up of hydroxyl ion concentration in the pores of the diaphragm occurs which readily mixes with the anolyte. Adverse potential gradient in the pores of the diaphragm is thus sufficient to prevent the reduction of iodate ion. Diaphragm used in this way is very effective and does not cause an excessive IR drop or polarization potential.

Pfeifer's process employs cornstarch as the raw material whereas we utilise indigenous tapioca starch as the raw material which is available in plenty in India. The process has also been tried for maize starch.

Thus, a concentrated solution of iodic acid was prepared by electrolytic oxidation of iodine or sodium iodide, using either graphite or electrodeposited lead dioxide (over graphite or carbon substrates) as anodes and using cathodes wrapped with diaphragm as described above. Iodic acid was oxidised to periodic acid at lead dioxide anodes and cathodes wrapped with diaphragm materials as described above (first stage). The periodic acid solution thus obtained was then reacted (second stage) with tapioca starch outside the cell to be oxidized to polymeric dialdehyde starch. After the reaction was complete, dialdehyde starch was removed from the electrolyte and washed thoroughly so that the spent electrolyte (containing iodic acid) was recycled through the electrolyzers for the regeneration of periodic acid. The process is described in detail in the following paragraphs:

Oxidation of iodic to periodic acid:

Iodic acid was oxidized to periodic acid in an electrolytic cell fitted with lead dioxide anodes and nickel-plated iron cathodes covered with asbestos cloth or ropes. When lead dioxide formed over lead was used as anode, the anode loss was about 2 to 2.5 g for 100 amp/hr and 1.62 g for 1 per cent silver-lead alloy, whereas the anode loss was about 0.2 to 0.3 g for 100 amp-hr by using lead dioxide electrodeposited on graphite as anode. The anodes and cathodes were mounted on a wooden support using a glass container as cell. Pre-electrolysis using the anode has been found to be important before the commencement of electrolysis. The electrolyte was agitated occasionally by an air-blower device. The concentration of iodic acid was kept between 2.5 and 10 per cent but a solution of 10 per cent concentration could give the maximum current efficiency and yield. The temperature of oxidation could vary from 25-45°C but a temperature of 35°C. was employed for most of the experiments. A current density of 2.5 amp/sq.dm. to 5.0 amp/sq.dm. could be employed. A current efficiency of 80 per cent and an yield of 94 per cent periodate was obtained by using a prepolarised lead dioxide formed over lead as anode and a pretransformed deposited lead dioxide anode (with graphite substrate) was found to give as good current efficiency as lead dioxide formed on lead itself. A quantitative conversion of iodic acid to periodic acid was obtained. After removing the suspended impurities, the periodic acid in the electrolyte was estimated and the solution pumped to the oxidation tank.

Oxidation of Tapioca starch by periodic acid:

Hard rubber buckets provided with glass cooling coils and air-blower device for agitation was used as oxidation tank. Oxidation could be carried out at 20°C. to 35°C the duration of oxidation being reduced at higher temperatures. The mole ratio of periodic acid to tapioca starch was varied from 1.0 to 1.25 and a mole ratio of 1.10 was found quite suitable for the purpose. The pH of the oxidant could be varied in the range 1 to 3.5, but a pH of 2.0 to 2.5 was found to be optimum. Keeping the mole ratio of periodic acid to starch as mentioned above, the concentration of periodic acid could be varied from 2.5 to 10 per cent but a 9 per cent solution at a temperature of 35°C. was found to be advantageous. The required quantity of tapioca starch was added and agitated by blowing air into the reactor. After the reaction was over, the oxidised starch was allowed to settle for about 2 hours and the clear supernatant liquid was syphoned to the electrolyser. The remaining slurry was filtered under suction or centrifuged and washed well with water. The filtrate was collected

and returned to the electrolyser for regeneration and the dialdehyde starch was dried in air. An overall current efficiency of 75 per cent was obtained with a dialdehyde content of 82 per cent in the product and an energy consumption of 5.1 kw-hr per kilogram of dialdehyde starch.

The presence of organic impurities in the spent electrolyte decreases the current efficiency for the regeneration of periodic acid. The spent purified electrolyte only is recirculated for regeneration of periodic acid.

EXAMPLES (Based on Small Scale Trials).

(a) Iodine to iodic acid (Iodide to Iodate):

150 g of sodium iodide or 127 g of iodine along with 40 g of sodium hydroxide was dissolved in 750 cc of distilled water containing 1.5 g. of sodium or potassium chromate. When lead dioxide formed on lead was used as anode, 25 g of sodium sulphate was added to the above solution. Either lead dioxide on lead or electrodeposited lead dioxide over graphite could be employed as anode. Stainless steel was used as cathode. During the oxidation, the temperature was kept between 40-45°C. and the pH was in the range of 8-9.5. A current density of 7.5 amp/sq.dm. (in the case of lead dioxide on graphite, 25 amp/sq.dm.) was employed and after passing 85 per cent of the theoretical current required (136 amp-hrs) the whole solution was cooled to the room temperature (30°C.) and the separated needle-shaped crystals washed well with distilled and dried. 97 g of sodium iodate crystallised out and 35 g was obtained in the mother liquor and thereby a conversion efficiency of 82 per cent was obtained. The mother liquor was preserved for subsequent runs.

(b) Iodic acid to Periodic acid (Iodate to Periodate):

(i) 200 g of sodium iodate was dissolved in 2 litres of distilled water containing 23 g of sulphuric acid. The pH of the electrolyte was 2.5 to 3.0 and the temperature was kept at 35-40°C. Lead dioxide was used as anode and nickel-plated iron cathode covered by asbestos rope was used as cathodes. No catholyte was used. The anodic current density was 5 amp/sq.dm. 180 g of periodic acid was obtained with a current efficiency of 50 per cent for a 90 per cent yield.

(ii) Iodic acid to Periodic acid (use of Nylon diaphragm): 20 g of sodium iodate was dissolved in 200 cc of distilled water containing 2 g of sulphuric acid. The pH of the electrolyte was 2.5-3.0 and the temperature was kept at 30-35°C. Lead dioxide was used as anode and stainless steel covered with nylon cloth was used as cathodes. No separate cathode chamber was used. The anodic current density was 5 amp/sq.dm. 17.9 g of sodium periodate was obtained with a current efficiency of 38 per cent for a 83 per cent yield.

(iii) Iodic acid to periodic acid (Use of nylon with asbestos diaphragm): The conditions are the same as described in (ii). The cathodes were first covered with asbestos and then nylon cloth was tightly fitted over it. 18.4 g of sodium periodate was obtained with a current efficiency of 42 per cent for 85 per cent yield.

(c) Oxidation of tapioca starch by periodic acid (Periodate):

275 g of periodic acid diluted to 3 litres was cooled to 30°C. and the pH was adjusted to 2.5. Then 275 g of tapioca starch (10% moisture) was added in portion with agitation. After the completion of the oxidation (4 hours), it was allowed to settle and the supernatant liquor was pumped to the electrolyser. During oxidation, periodic acid was converted to iodic acid. Then the sludge was centrifuged and washed well with distilled water. The dialdehyde starch was dried in air and powdered. 230 g of dialdehyde starch with a dialdehyde content of 82 per cent was obtained. The wash water after concentration, was sent to the electrolyser for the regeneration of periodic acid and an overall current efficiency of 77 per cent was obtained for dialdehyde starch formation. The experiments were continued with the same electrolyte and in the second, third and fourth runs, 252 g, 250 g, and 220 g of dialdehyde starch was obtained giving overall current efficiency of 75 per cent, 74.8 per cent and 65 per cent respectively.

LARGE LABORATORY SCALE TRIALS

The apparatus used for the large laboratory scale preparation of iodic acid is shown in the three sheets of the

accompanying drawings. Fig. 1 is the cell for the preparation of iodic acid from iodine (iodate from iodide). A in Fig. 1 is the sectional front elevation of the cell tank and B in Fig. 1 is the sectional end elevation of the cell tank. A porcelain rectangular tank of dimensions 59 cm length, 35 cm breadth and 25 cm height was used as a cell. Four electrodeposited lead dioxide electrode on graphite substrate of dimensions 31 cm length, 16 cm breadth and 1.6 cm thickness with an effective area of 15 sq.dm. were used as anodes and the whole anode assembly is shown in C, Fig. 2. The end elevation of anode is shown in D, Fig. 2. Ten stainless steel plates of dimensions 26 cm length, 3 cm breadth and 0.1 cm thickness were first covered with asbestos fibre and finally covered with nylon bags were used as cathodes. The whole cathode assembly is shown in C, Fig. 1. The end elevation of the cathode is shown in D, Fig. 1. The cell was provided with stainless steel cooling coils to maintain the temperature by the circulation of cold water and suitable wooden lid as shown in Fig. 3, carrying the necessary holes for the anode assembly, cathode assembly, cooling coils and thermometer. A in Fig. 3 represents the front elevation and B in Fig. 3 shows the plan of the lid.

The cell set-up for the preparation of periodic acid from iodic acid (periodate from iodate) is shown in Fig. 2. A in Fig. 2 represents the sectional front elevation of the cell tank and B in Fig. 2 shows the sectional end elevation. A porcelain rectangular tank of dimension 59 cm length, 42 cm breadth and 39 cm height was employed as the cell so as to handle 64 litres of the electrolyte. The anode assembly and cathode are quite similar to those employed for the preparation of iodic acid from iodine (iodate from iodide) as shown in C and D in Fig. 1 and C and D in Fig. II. A stainless steel cooling coil was used to maintain the temperature.

EXAMPLES (Based on Large Laboratory Scale Trials).

A) Iodine to iodic acid (Iodide to Iodate): 6.35 kg of crude iodine along with 2 kg of sodium hydroxide (Tech) was dissolved in 20 litres of distilled water. During the oxidation the temperature was kept between 45-55°C. and the pH was in the range of 10-12. A current density of 15 amp/sq.dm. was employed and after passing 80 per cent of the theoretical current required (6.4 kilo-amp-hrs) the whole solution was cooled to room temperature (30°C.) and the solid separated, washed well with distilled water and dried. 4.74 kg of sodium iodate crystallised out and 1.472 kg was obtained in the mother liquor and thereby a conversion efficiency of 85 per cent was obtained. The mother liquor was preserved for subsequent runs.

B) Iodic acid to Periodic acid (Iodate to Periodate):

i) 1.375 kg of sodium iodate was dissolved in 22 litres of distilled water and the pH of the electrolyte was adjusted to 2.5-3.0 by means of dilute sulphuric acid. The temperature was kept at 30-35°C. Lead dioxide (Fig. 2C) was used as anodes and stainless steel covered with asbestos-nylon cloth was used as cathodes (Fig. 1C). No separate cathode chamber was used. The anodic current density was 5 amp/sq.dm. Occasionally the electrolyte was agitated by means of bubbling air. 1.170 kg of sodium periodate was obtained with a current efficiency of 47.2 per cent for a 88.7 per cent yield.

ii) 4.353 kg of sodium iodate was dissolved in 60 litres of distilled water and the pH was adjusted to 3.0 by means of sulphuric acid. All the other conditions were the same as in (i). 2.172 kg of sodium iodate was obtained with a current efficiency of 38 per cent for a yield of 55 per cent.

C) Oxidation of tapioca starch by periodic acid (Periodate):

i) 1.170 kg of sodium periodate diluted to 20 litres was cooled to 25°C. and the pH was adjusted to 2.5. Then 1.20 kg of tapioca starch (10% moisture) was added in portion with agitation. After the completion of the oxidation (4 hours) it was allowed to settle and the supernatant liquor was pumped to the electrolyser. During oxidation, periodic acid was converted to iodic acid. Then the sludge was centrifuged and washed well with distilled water. 1.20 kg of dialdehyde starch with a dialdehyde content of 85 per cent was obtained. The wash water

after concentration, was sent to the electrolyser for the regeneration of periodic acid.

ii) 2.772 kg of periodic acid diluted to 60 litres was cooled to 30°C. and the pH was adjusted to 2.5. Then 2.07 kg of maize starch (10 per cent moisture) was added in portions and all the other procedures were the same as in (i). 2 kg of dialdehyde starch with a dialdehyde content of 85 per cent was obtained.

We claim

1. A process for the electrochemical production of dialdehyde starch by (i) the electrolytic oxidation of iodic acid to periodic acid (first stage), followed by (ii) oxidation of tapioca starch or like starch material by periodic acid (second stage) which is characterised in that the electrolytic oxidation of iodic acid is carried out in a cell in which lead or 1% lead-silver alloy on which lead dioxide has been formed or electrodeposited lead dioxide having graphite or carbon substrate or without a substrate, are used as anodes, and cathodes closely wrapped with asbestos cloth or rope or nylon cloth are used.

2. A process as claimed in Claim 1 wherein the iodic acid for the preparation of periodic acid is prepared by electrolytic oxidation of iodine using lead dioxide formed on lead or lead alloys or electro-deposited lead dioxide as anodes and using stainless steel as cathode.

3. A process as claimed in Claim 1 or 2 wherein iodic acid is prepared by electrolytic oxidation of iodine using graphite anode and using stainless steel as cathode.

4. A process as claimed in Claim 1 wherein stainless steel, iron, nickel or nickel-plated copper, nickel-plated iron or nickel-plated brass wrapped with asbestos cloth or rope are used as cathodes.

5. A process as in Claim 1 wherein a current density of 1 to 10 amp/sq.dm but preferably 5 amp/sq dm. and a temperature range of 30-45°C but preferably 35-40°C. and a pH of 1 to 4 but preferably 2.5 to 3 are employed to obtain quantitative conversion of iodic acid to periodic acid in the first stage.

6. A process as in Claim 1 wherein the solution of periodic acid obtained in the first stage from the electrolytic cell is allowed in the second stage to react with either tapioca starch or any other like starch material by agitation in a separate reactor.

7. A process as in Claim 6 wherein the oxidation of starch is carried out at a temperature of 20 to 35°C, but preferably at 25°C.

8. A process as in Claim 6 wherein a mole ratio of starch to periodic acid of 1 to 1.5 is used for the oxidation reaction.

9. A process as in Claim 6 wherein the pH of the periodic acid during oxidation of starch is kept within the range of 1 to 3.5 but preferably at 2.5.

10. A process as in Claim 6 wherein dialdehyde starch formed is recovered by centrifuging or filtration under suction and washed well with water to free dialdehyde starch from electrolyte.

11. A process as in Claims 1 to 10 wherein the process of oxidation of iodine to periodic acid in the first stage, oxidation of tapioca starch or any other like starch material to dialdehyde starch in the second stage and the regeneration of periodic acid from iodic acid followed by subsequent oxidation of further amount of starch is made cyclic.

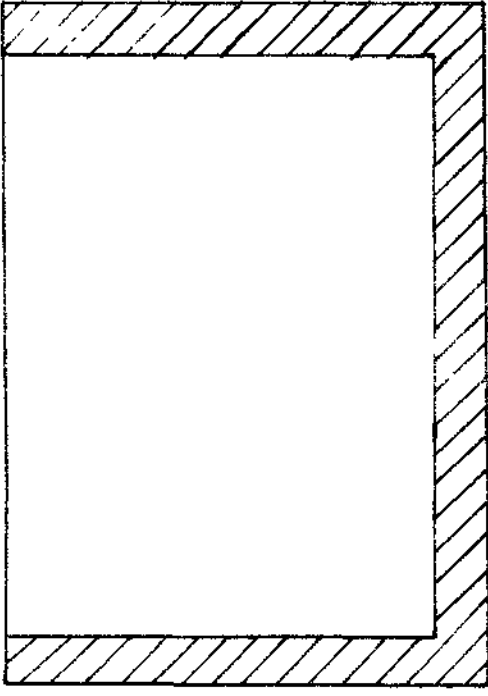
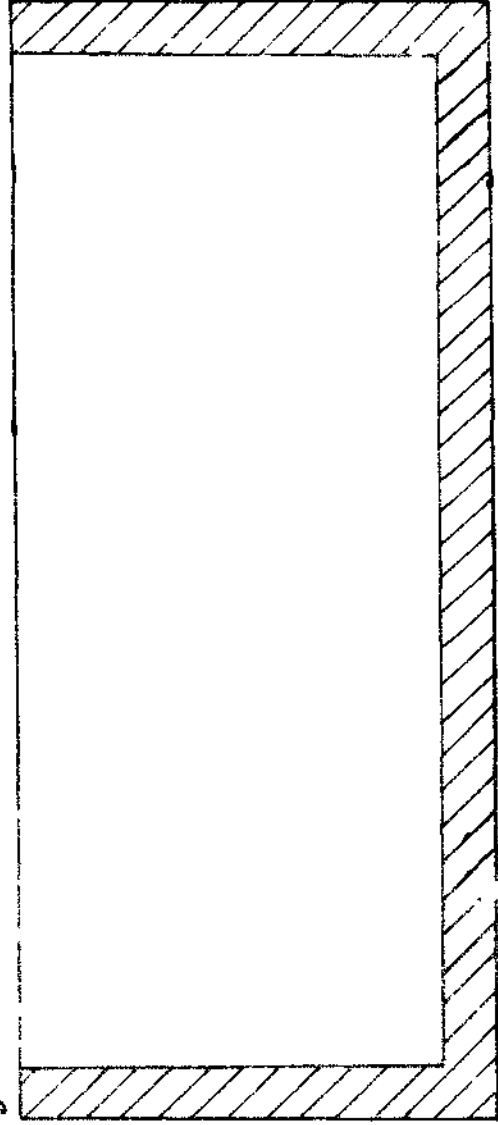
12. Dialdehyde starch from either tapioca starch or any other like starch material whenever prepared according to the process substantially as hereinbefore described.

R. BHASKAR PAI,

Patents Officer,

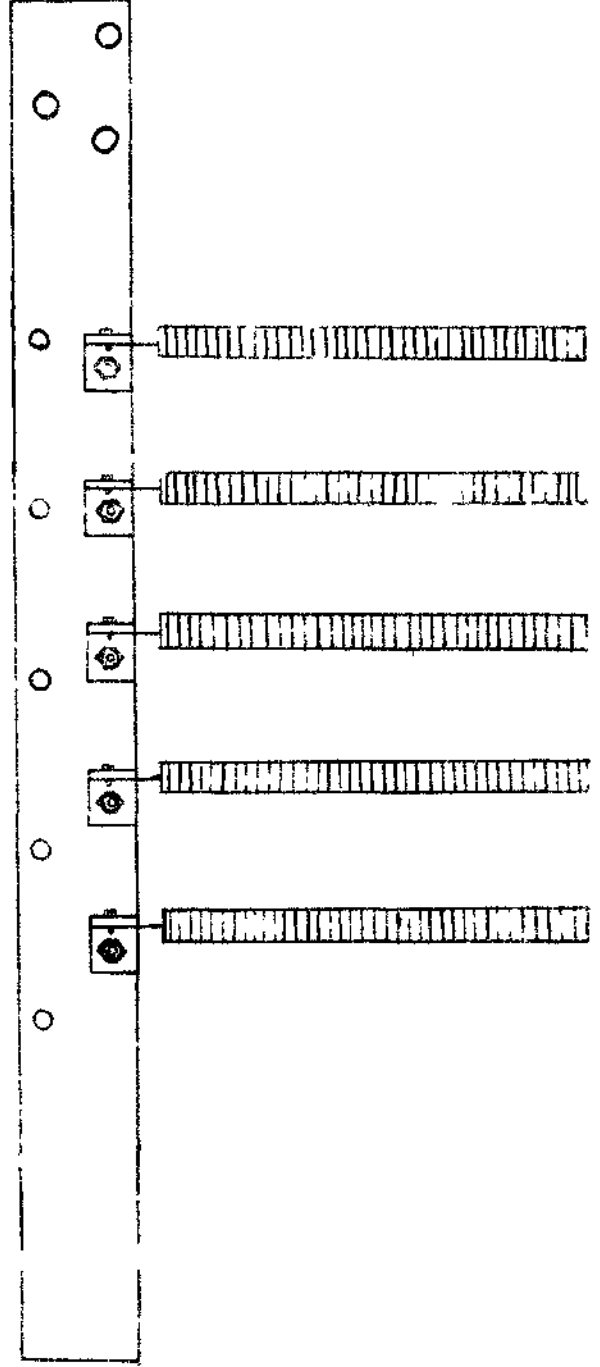
Council of Scientific and Industrial Research.

Dated this 23rd day of July 1962.

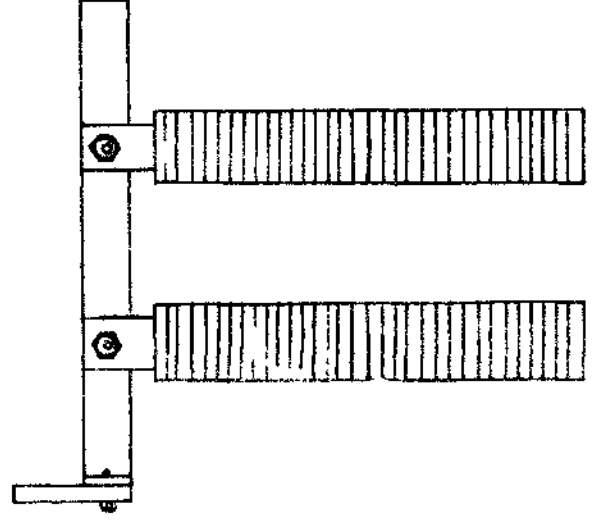


A

B

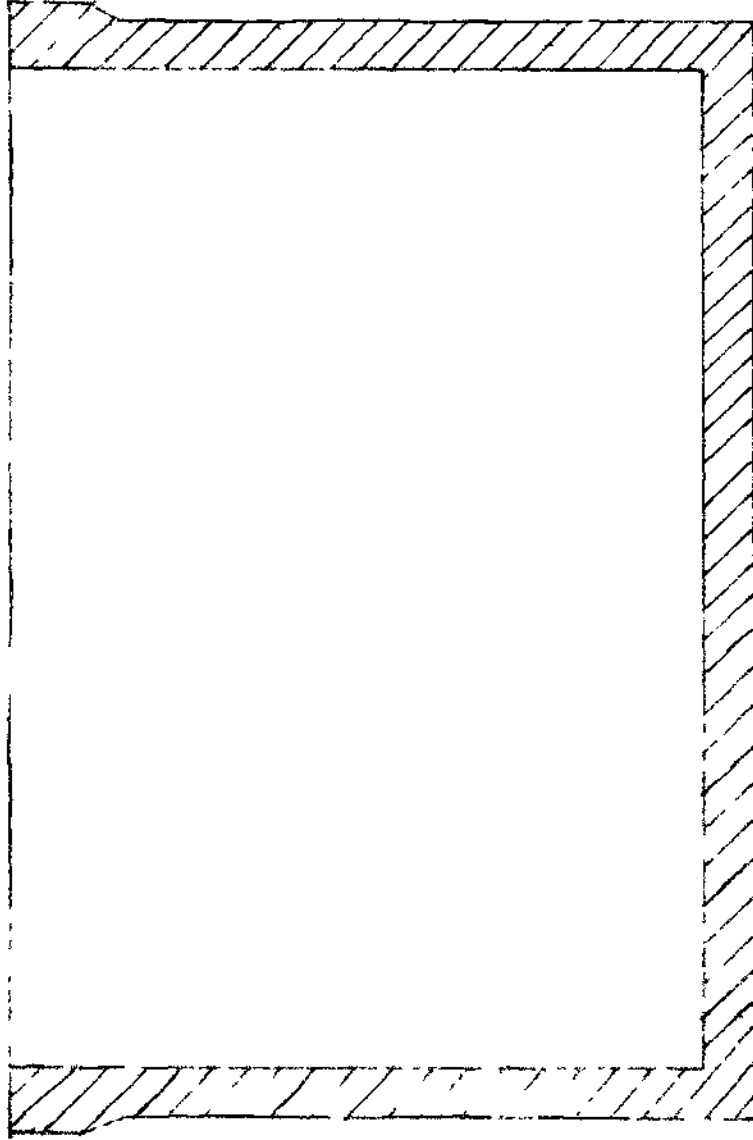


C

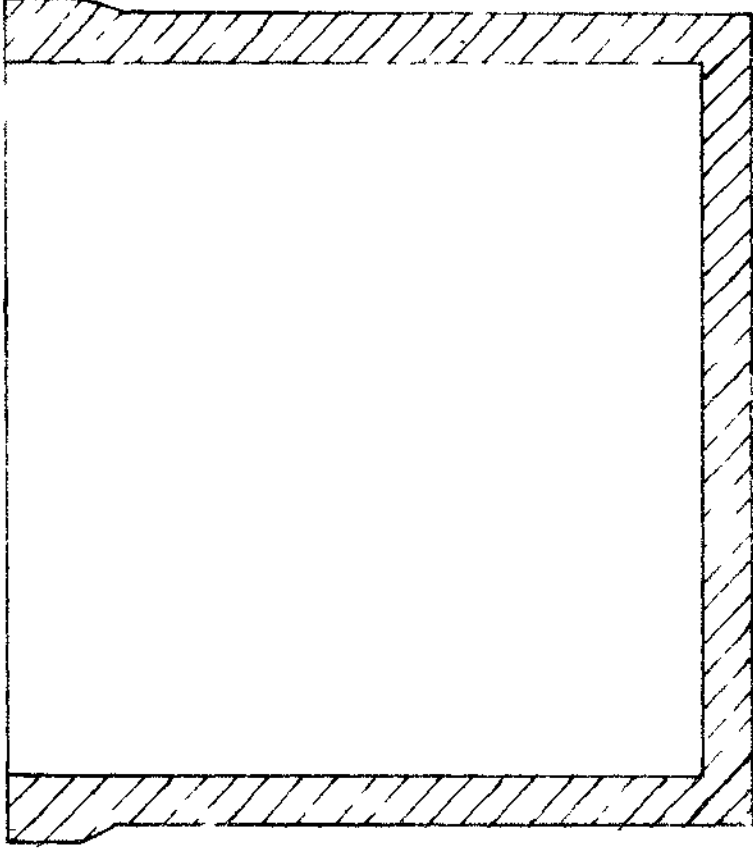


D

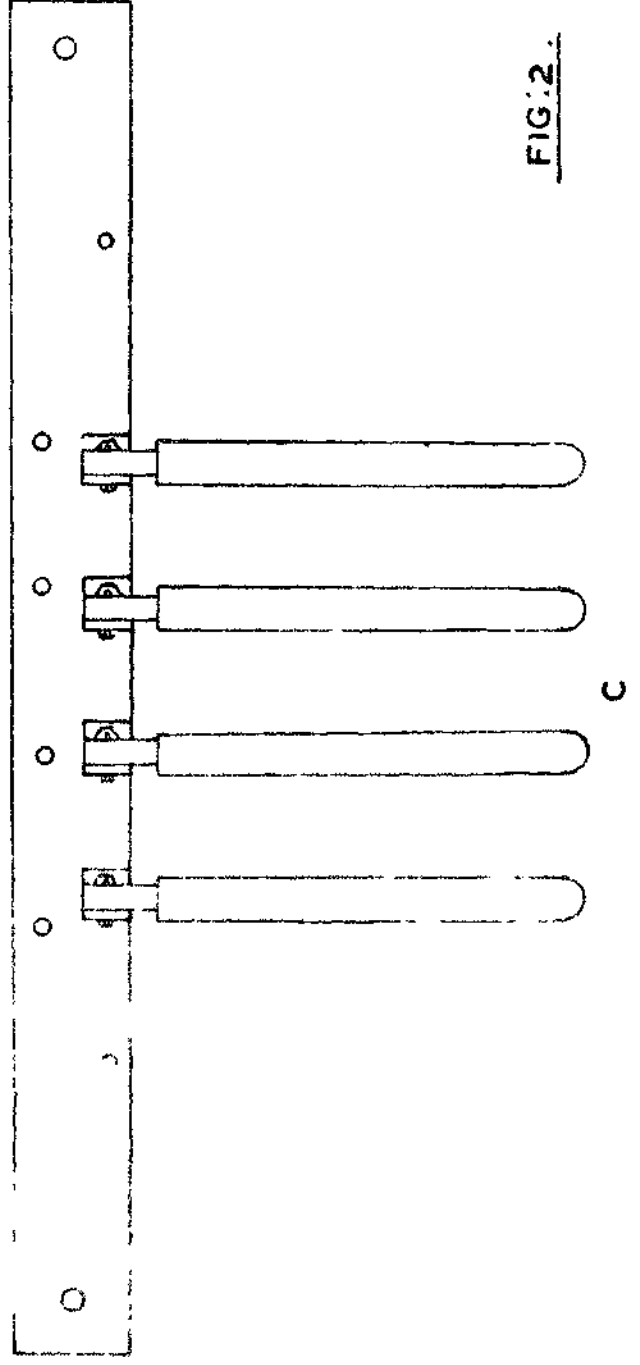
FIG. 1.



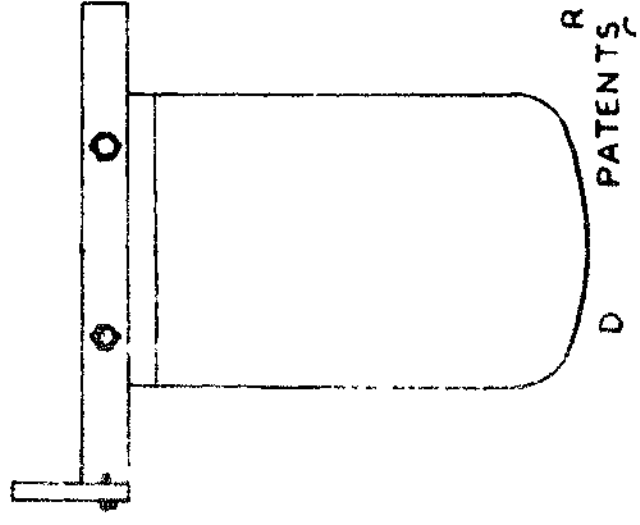
A



B



C



D

FIG:2.

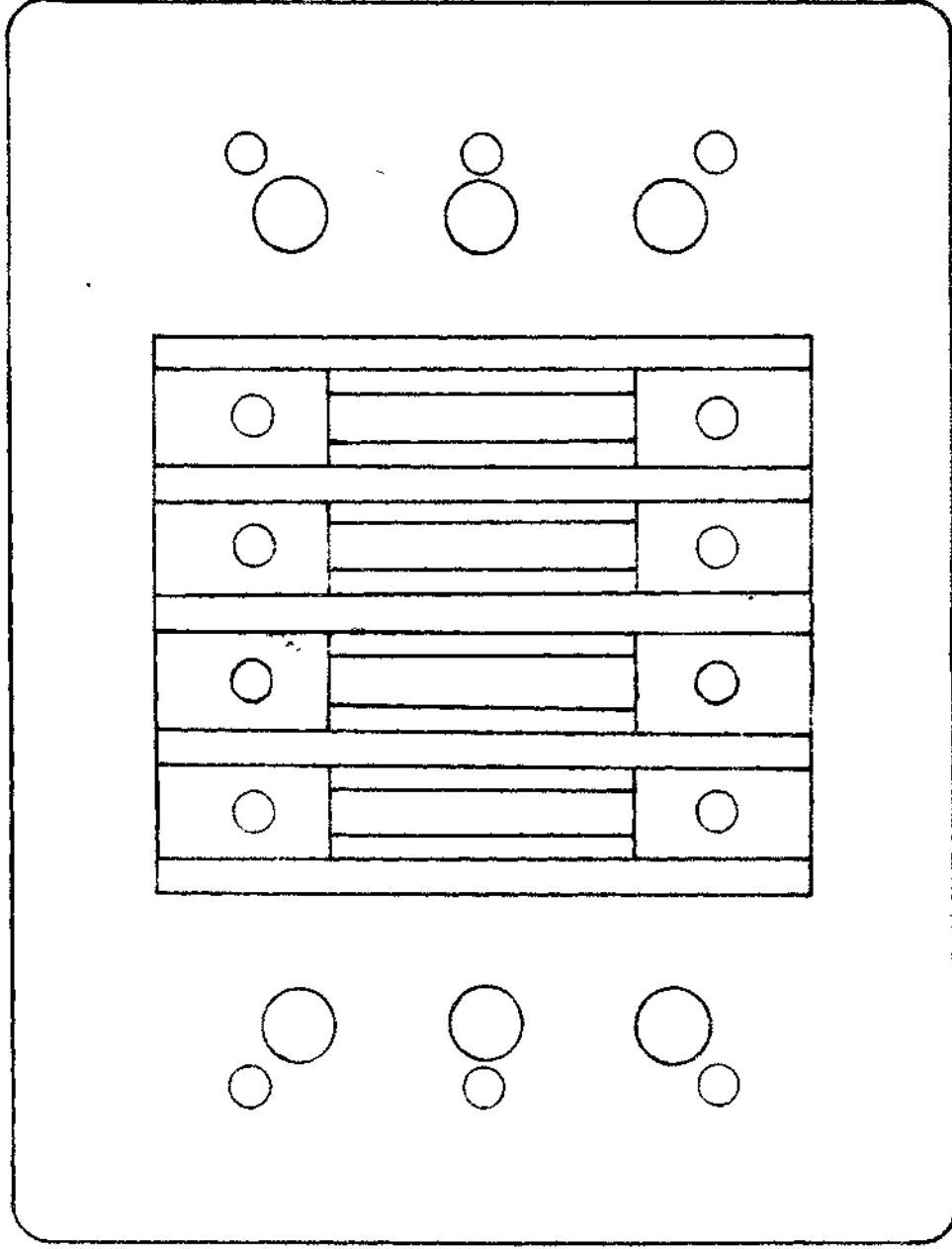
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INDUSTRIAL RESEARCH.

NO. 79075

THREE SHEETS.
SHEET NUMBER THREE.



A



B

FIG:3.

R.B.PAI.
PATENTS OFFICER
C.S.I.R.