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

Specification No. 66195. Application No. 66195, dated 22nd December 1958. Complete Specification left on 22nd September 1959. (Application accepted 21st June 1960.)

PROVISIONAL SPECIFICATION.

PREPARATION OF LEAD DIOXIDE ELECTRODES FOR ELECTROLYSIS.

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 and KAPISTHALAM CHETTLUR NARASIMHAM, both of the Central Electrochemical Research Institute, Karaikudi, India, both Indian citizens.

Lead dioxide could be deposited from soluble salts of lead in aqueous solution, is known from a very long time. In recent years interest in this has grown very much and a considerable amount of work has been done in obtaining lead dioxide deposits in a suitable way so as to use them as electrodes, especially as anodes in electrolytic oxidations. Concentrated solution of lead nitrate has been suggested as electrolyte containing copper nitrate also as one of the baths from which lead dioxide could be deposited. Several metals have been used by various people on which lead dioxide deposition could be tried. Reference is also available to the fact that lead dioxide deposits on graphite also.

In the preparation of these electrodes, a serious defect reported and observed by the present workers also is that the deposit obtained is highly porous and unless sufficiently thick deposits are prepared, the deposited lead dioxide cannot be used as electrodes. Several means of avoiding pinholes by the addition of suitable surface active agents, ionic and non-ionic have been described in order to obtain smooth deposits without pinholes.

Attempts made so far have been to separate the lead dioxide deposited from the basis material so that directly it could be used as electrodes. Making of electrical contacts on lead dioxide has always been a problem and several patents have been taken out for the same. Using the metal core itself for the lead dioxide deposit for contact and using in electrolysis has been reported to be a failure because of the porosity of the deposit and dissolution of basis metal.

The present invention takes into consideration all the various difficulties that are encountered in the preparation of lead dioxide electrodes and describes a technique whereby it is possible to obtain the electrodes which can be used with advantage in various electrolytic processes. The technique consists in rotating the electrodes, in the preparation of cylindrical electrodes and giving a to-and-fro motion to the same in the preparation of plate electrodes. In the deposition of lead dioxide from nitrate bath, free nitric acid is formed at the anode and this is neutralized by the addition of either copper carbonate or lead carbonate or lead monoxide (Litharge) or lead hydroxide. The carbon dioxide gas bubbles form at the electrode surface also, during the addition of carbonates and a porous deposit is normally obtained. No amount of stirring the electrolyte can change this state of affairs. Movement of the anode in the way described, not only favours dislodging of the gas bubbles from the surface but also favours the dissipation of the nitric acid formed into the bulk of the electrolyte. The deposit obtained is thus free from pores and the deposit is quite adherent and compact, having a smooth surface without any lump formation, especially at the edges in the preparation of plate electrodes.

The other important step is the use of graphite as basis material for deposition of lead dioxide. Not only very adherent and smooth deposit free from pores are obtained, but graphite itself can be retained as the core and electrical connection made on the same. Only the portion of the electrode covered with lead dioxide is immersed in the electrolyte in regular electrolysis. It is possible to obtain a thin deposit on graphite so that the graphite is effectively protected from disintegration also. Deposits upto 1 cm thick or more can also be obtained on graphite by the above technique. Thus, deposition of lead dioxide on graphite serves a double purpose, (a) by effecting electrical contact to lead dioxide electrode by graphite itself and (b) by protecting the graphite from disintegration.

In case the deposit cracks by use the surface of graphite could be again smoothed out and lead dioxide deposited once more. The graphite core inside the lead dioxide deposit is not objectionable, as metal cores have been reported to be, because even if graphite is attacked it will not introduce harmful impurities to the bath.

The invention may therefore be stated as follows. Lead dioxide is deposited on graphite anode which is kept (a) rotating for cylindrical electrodes or (b) given a to-and-fro motion for plate electrodes from a bath containing soluble salts of lead and copper, preferably lead nitrate, so as to give smooth, adherent deposits free from pinholes and lumps.

ELECTROLYSIS

Solution containing 380 g/l lead nitrate and 20 g/l copper is the electrolyte. Graphite rods which have been thoroughly cleaned by making them anodes in alkali and electrolyzing for 3 to 5 minutes at 10 amp/dm<sup>2</sup> and washing, are dried and used as anodes. 4 strips of copper all connected at the lower end so as to form a cage like arrangement served as cathode and favoured proper current distribution on the anode. The anode was rotated at an r.p.m. varying from 500 to 2500 or above (15.7 meters/min. to 78.5 meters/min. peripheral velocity). Other conditions of electrolysis were studied and temperature from 30°-80°C could be used, pH of the bath was maintained between 1.5 to 5.0. Anode current density of 1 to 12 amps/dm<sup>2</sup> could be employed and during electrolysis, the nitric acid is neutralized either by the addition of lead carbonate or lead monoxide or lead hydroxide and suitable amount of copper carbonate. Copper is deposited on the copper cathode and could be redissolved in nitric acid and used either as copper nitrate or as copper carbonate by precipitating the same from copper nitrate. The current efficiency for all the experiments were very nearly quantitative on the basis that two Faradays of electricity are required to deposit a mole of lead dioxide.

In the case of plate electrodes, an arrangement for a to-and-fro moving horizontal shaft was got fabricated. This shaft had a central slot through which the plate electrodes could be suspended. Two cathodes on either side of the anode were used. In addition to the to-and-fro movement of the plate anode, a stirrer was also employed, to effectively react the lead carbonate with the acid in the electrolyte.

EXAMPLES

(i) Preparation of cylindrical electrodes: 600 cc of electrolyte was taken in a 1-litre tall form beaker. 1 cm diameter graphite rod was rotated at 1500 r.p.m. The anode current density was 6 amp/dm<sup>2</sup>. Depositions were carried out for 4, 6 and 8 hours respectively. The weight of the deposits obtained were 30.1, 40.7 and 58.5 g respectively. The temperature was 30°C. The deposits were quite adherent, smooth and shining. The current efficiencies were almost quantitative and the electrodes quite suitable for use in other processes.

The electrode prepared under exactly similar conditions but keeping the anode stationary were full of holes even after 6 hours of deposition.

(ii) Graphite rods 1" in diameter and nearly 10" long were similarly used and lead dioxide deposited on the same.

Preparation of plate electrodes: (i) In an oval glazed porcelain tank, 3 litres of electrolyte was taken. A graphite plate anode 15 cm x 5 cm was attached on to the to-and-fro moving shaft which was moving along the longer axis of the oval vessel with about 1.5" displacement. Two

Price : TWO RUPEES.

copper cathode strips of the same dimensions as the anode are used on either side. Deposition at 2.5 amp was carried out for 2 hours and 4 hours using the to-and-fro motion of the anode. An adherent smooth deposit free from any nodules at the edges was obtained to a height of 13 cm on the anode. Deposit obtained keeping the plate stationary, had many pinholes even though the current efficiency was quantitative in both the cases.

(ii) Similarly, deposition of lead dioxide was carried out for 2 hours at higher current density (5 amp/dm<sup>2</sup>) to give deposit which was very adherent and smooth.

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Dated this 10th day of December 1958.

## 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 1860).

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 and KAPISTHALAM CHETTLUR NARASIMHAM, both of the Central Electrochemical Research Institute, Karaikudi, India, both Indian citizens.

This invention relates to the preparation of lead dioxide electrodes for electrolysis.

The use of several types of baths containing soluble salts of lead under both acidic and alkaline conditions for the deposition of lead dioxide has been recommended in literature by earlier workers. In recent years, interest in the use of lead dioxide electrodes has been very much in evidence and a considerable amount of work has been carried out to obtain lead dioxide deposits in a suitable form so as to use them as anodes in electrolysis. The most important among the different baths used so far is the one consisting of a concentrated solution of lead nitrate containing small amounts of copper nitrate also. In this bath, the acid liberated is normally neutralised by the addition of lead carbonate. Lead monoxide and lead hydroxide can also be used for the same purpose. Copper deposited from the bath is replenished by the addition of copper carbonate.

In the preparation of lead dioxide electrodes, a serious difficulty reported earlier and also observed by the present workers is that the deposit obtained on stationary anodes is highly porous and unless sufficiently thick deposits are prepared the deposited lead dioxide cannot be used as an anode. Several means of avoiding pinholes and a porous deposit by the addition of suitable surface active agents, ionic and non-ionic have been described in literature.

Earlier workers have attempted to separate the lead dioxide deposited on a base material so that the lead dioxide could be directly used as an anode by providing suitable electrical contact for the same. The electrodes used under such cases have been sufficiently thick, massive and heavy and would normally be expensive also, involving high energy consumption for their preparation.

When it is not intended to separate the lead dioxide from the base material on which it is deposited, attempts have been made to deposit lead dioxide on a base material which will not normally be attacked either during deposition or during its use as an anode in the electrolysis. The base material used by such investigators consists of tantalum, platinum, nickel or platinum-clad-tantalum which are highly expensive metals. Whenever the lead dioxide deposit has been removed from the basis material such as nickel or iron, the making of electrical contact on the lead dioxide has proved a difficult problem and several processes have been worked out for successful methods of providing the same. A few attempts by earlier workers to leave the lead dioxide deposit on other metals as base material for providing the electrical contact has proved a failure in actual practice during electrolysis, because the base material had itself dissolved and introduced harmful impurities into the electrolyte.

The present invention takes into consideration the various difficulties that are encountered in the preparation of lead dioxide electrodes and describes the technique adopted whereby it is possible to obtain electrodes which can be used with advantage in various electrolytic processes.

The present invention for the preparation of lead dioxide electrodes consists in electrolytically depositing lead dioxide on graphite and/or carbon base material

anodes, using copper cathodes, from baths containing soluble salts of lead, preferably from lead nitrate bath.

The salient features which distinguish the present practice as a unique technique of obtaining lead dioxide electrodes suitable for electrolytic oxidations are given below:

(a) Lead dioxide is deposited from any of the baths containing soluble salts of lead, on either stationary, rotating or to-and-fro moving anodes of graphite and/or carbon so that the graphite and/or carbon themselves act as a means of providing electrical contact for the lead dioxide deposit. The graphite and/or carbon cores also act as the lead for the current and they also act as support for the deposited lead dioxide so that it is possible to obtain deposits of any thickness to suit the purpose thereby avoiding the need for providing any other type of electrical contact. Thus lead dioxide can be deposited on stationary graphite and/or carbon base materials at low current densities (0.1 to 3 amp/dm<sup>2</sup>) and on moving electrodes at current densities up to 15 amp/dm<sup>2</sup>. Lead dioxide electrodes can be prepared by depositing the same even in very thin layers (0.1 mm to 2 mm) on graphite and/or carbon base materials.

(b) When lead dioxide is deposited on stationary graphite and/or carbon anodes from suitable baths containing soluble salts of lead, either ionic or non-ionic wetting agents may be added to the bath to obtain deposits free from pores and pinholes. To obtain smooth, adherent and compact deposit of lead dioxide, the technique of rotation of the anode to obtain cylindrical anodes and of giving a to-and-fro motion in the preparation of plates may also be adopted.

(c) The electrodes thus prepared having the facility of proper electrical contact serve the purpose of the use of these as lead dioxide anodes in electrolysis even in reactions where graphite is attacked and disintegration takes place so that this technique of depositing lead dioxide on graphite and/or carbon acts as an effective means also of preventing the disintegration of graphite and/or carbon.

(d) Even if there are any pinholes or flaws in the deposit of lead dioxide on graphite and/or carbon, the basis material is not attacked to the same extent and does not introduce harmful impurities to the bath as metal base materials would do during the electrolysis using such electrodes.

(e) If the deposited lead dioxide cracks or after some time comes off the basis material of graphite and/or carbon it is possible to remove the same completely and re-deposit lead dioxide on it once again so as to restore the original dimensions of the electrode by depositing a thicker coating of the same.

The present invention may therefore be stated as follows:

Lead dioxide is deposited (a) on graphite and/or carbon anodes as basis material (b) kept stationary, or rotated for the preparation of cylindrical electrodes or moved to-and-fro for the preparation of plate electrodes from a bath containing soluble salts of lead and copper, preferably

from lead nitrate and copper nitrate baths so as to give a smooth, adherent and compact deposit. Lead carbonate or lead monoxide and copper carbonate are added to the electrolyte to neutralise the nitric acid formed simultaneously.

### ELECTROLYSIS

Solution containing 300 g/l to 500 g/l lead nitrate and 20 g/l copper nitrate is the electrolyte. Graphite or carbon rods which have been thoroughly cleaned by making them anodes in alkali and electrolyzing for 3 to 5 minutes at 10 amp/dm<sup>2</sup> and giving acid dip in dilute nitric acid (10%) and washing, are dried and used as anodes. 4 strips of copper all connected at the lower end so as to form a cage like arrangement served as cathode and favoured proper current distribution on the anode. The anode was rotated at r.p.m. varying from 500 to 2500 or above (15.7 meters/min. to 78.5 meters/min. peripheral velocity). Other conditions of electrolysis were studied and temperature from 25°-80°C could be used, pH of the bath was maintained between 1.0 to 5.0. Anode current density of 0.2 to 12 amp/dm<sup>2</sup> could be employed and during electrolysis, the nitric acid was neutralised either by the addition of lead carbonate or lead monoxide or lead hydroxide and copper carbonate or cupric hydroxide equivalent to the amount of copper removed from the bath by deposition on the cathode during electrolysis. Copper is deposited on the copper cathode and could be redissolved in nitric acid and used either as copper nitrate or as copper carbonate by precipitating the same from copper nitrate. The current efficiency for all the experiments were very nearly quantitative on the basis that two Faradays of electricity are required to deposit a mole of lead dioxide.

In the case of plate electrodes, an arrangement for a to-and-fro moving horizontal shaft (A) was got fabricated (Sheet No. 1, Fig. 1 and 2 of accompanying drawings). Fig. 1 represents the side view of the apparatus and Fig. 2 represents the top view of the same. The shaft had a central slot (S) through which the plate electrodes (B) could be suspended. Two cathodes on either side of the anode were used. The to-and-fro movement was brought about by connecting the shaft to a crank wheel (C) which was run by a motor (M) by means of a pulley (P). In addition to the to-and-fro movement of the plate anode, a stirrer was also employed to effectively react lead carbonate with the acid formed in the electrolyte.

### EXAMPLES

#### (a) Preparation of cylindrical electrodes:

##### Rotating anodes:

(i) 600 cc of electrolyte was taken in a 1-litre tall form beaker. 1 cm diameter graphite rod was rotated at 1500 r.p.m. The anode current density was 6 amp/dm<sup>2</sup>. Deposits were carried out for 2, 4, 6, and 8 hours respectively. The weight of the deposits obtained were 15.05, 30.1, 40.7 and 58.5 g respectively. The temperature was 30°C. The deposits were quite adherent, smooth and shining. The current efficiencies were almost quantitative and the electrodes quite suitable for use in other processes. The average thickness of the deposits were 0.48, 0.95, 1.3, 1.8 mm for the corresponding experiments.

The electrodes prepared under exactly similar conditions but keeping the anode stationary were full of holes even after 6 hours of deposition.

(ii) Graphite rods 1" in diameter and nearly 10" long were similarly used and lead dioxide deposited on the same at about 800 to 1000 r.p.m. for 2 hours. The average thickness of the deposit was 0.5 mm.

(iii) Similarly on a 1 cm diameter graphite rod, lead dioxide was deposited for half-an-hour to give a thin, uniform, adherent and smooth coating at a current density of 6 amp/dm<sup>2</sup> at room temperature. The average thickness of the deposit was 0.1 mm.

(iv) Deposit of lead dioxide were also obtained on carbon rods of 1" diameter by electrolyzing lead nitrate for half-an-hour and 2 hours respectively. The efficiencies

were almost quantitative and average thickness of the deposits were 0.1 mm, 0.5 mm respectively.

##### Stationary anodes:

(v) Bath containing 380 g/l lead nitrate and 20 g/l copper nitrate was used at 30°C. A cylindrical (1 cm diameter) graphite rod was used as anode with a cage like cathode referred to earlier. Current density was 6 amp/dm<sup>2</sup> and the current concentration was 2.3 amp/litre (or lower). Deposition was carried out for half-an-hour (a) without addition agent and (b) with Teepol (1 cc per litre) as addition agent. The deposition efficiency was quantitative and a thickness of 0.1 mm of deposit was obtained in each case.

##### (b) Preparation of plate electrodes:

(i) In an oval glazed porcelain tank, 3 litres of electrolyte was taken. A graphite plate anode (B) 15 cm x 5 cm was attached on to the to-and-fro moving shaft (A) which was moving along the longer axis of the oval vessel with about 1.5" displacement. Two copper cathodes of suitable dimensions are used on either side. Deposition at 2.5 amp was carried out for 2 hours and 4 hours using the to-and-fro motion of the anode (1000 to 1200 times/minute). An adherent smooth deposit free from any nodules at the edges was obtained to a height of 13 cm on the anode. Deposit obtained keeping the plate stationary, had many pinholes even though the current efficiency was quantitative in both the cases.

(ii) Similarly, deposition of lead dioxide was carried out for 2 hours at higher current density (5 amp/dm<sup>2</sup>) to give deposit which was very adherent and smooth.

##### We claim:

1. A process for the preparation of lead dioxide electrodes which consists in electrolytically depositing lead dioxide on graphite and/or carbon base material anodes, using copper cathodes, from baths containing soluble salts of lead, preferably from lead nitrate bath.

2. A process as claimed in Claim 1 wherein the anode is kept stationary or rotated for obtaining cylindrical anodes and moved to-and-fro for preparing plate-type anodes.

3. A process as claimed in Claim 2 wherein lead dioxide is deposited on stationary graphite and/or carbon base materials at low current densities (0.1 to 3 amp/dm<sup>2</sup>) and on moving electrodes at current densities upto 15 amp/dm<sup>2</sup>.

4. A process as claimed in any of the preceding claims wherein a bath containing 300 to 500 g/l lead nitrate, 20 g/l copper nitrate at a temperature of 25°C to 80°C and a current density of 0.1 to 15 amp/dm<sup>2</sup> and a bath pH of 1 to 5 is employed and the nitric acid formed is neutralised by lead hydroxide, lead monoxide or preferentially by lead carbonate and copper carbonate.

5. A process as claimed in any of the preceding claims wherein rotation of the anode to obtain cylindrical electrodes and to-and-fro motion to obtain plate type anodes are employed wherein a peripheral velocity of 15 to 80 meters/minute or above is employed for the electrodes so as to obtain a smooth, adherent, uniform and shiny deposit.

6. A process as claimed in any of the preceding claims wherein the copper deposited on the cathode is dissolved in nitric acid so as to obtain copper nitrate which could be directly used or used as copper carbonate by precipitating the same from copper nitrate.

7. A process as claimed in any of the preceding claims wherein graphite and/or carbon cores are employed as current leads, thereby providing proper electrical contact for the deposited lead dioxide.

8. A process as claimed in any of the preceding claims wherein lead dioxide electrodes are prepared by depositing the lead dioxide in very thin layers (0.1 mm to 2 mm) on graphite and/or carbon base materials which act as support for the same.

9. A process as claimed in any of the preceding claims wherein unattackable and non-disintegrating graphite and/or carbon electrodes are prepared by depositing lead dioxide on graphite and/or carbon base material.

10. A process as claimed in any of the preceding claims wherein the graphite and/or carbon cores from which the deposit is cracked and peeled off could be re-used by again depositing lead dioxide on the said graphite and/or carbon cores.

11. A process for the preparation of lead dioxide

electrodes on graphite and/or carbon base materials as substantially hereinbefore described.

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*Dated this 27th day of August, 1959.*

COMPLETE SPECIFICATION

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

NUMBER OF SHEETS ONE  
SHEET NUMBER ONE

No. 66195.

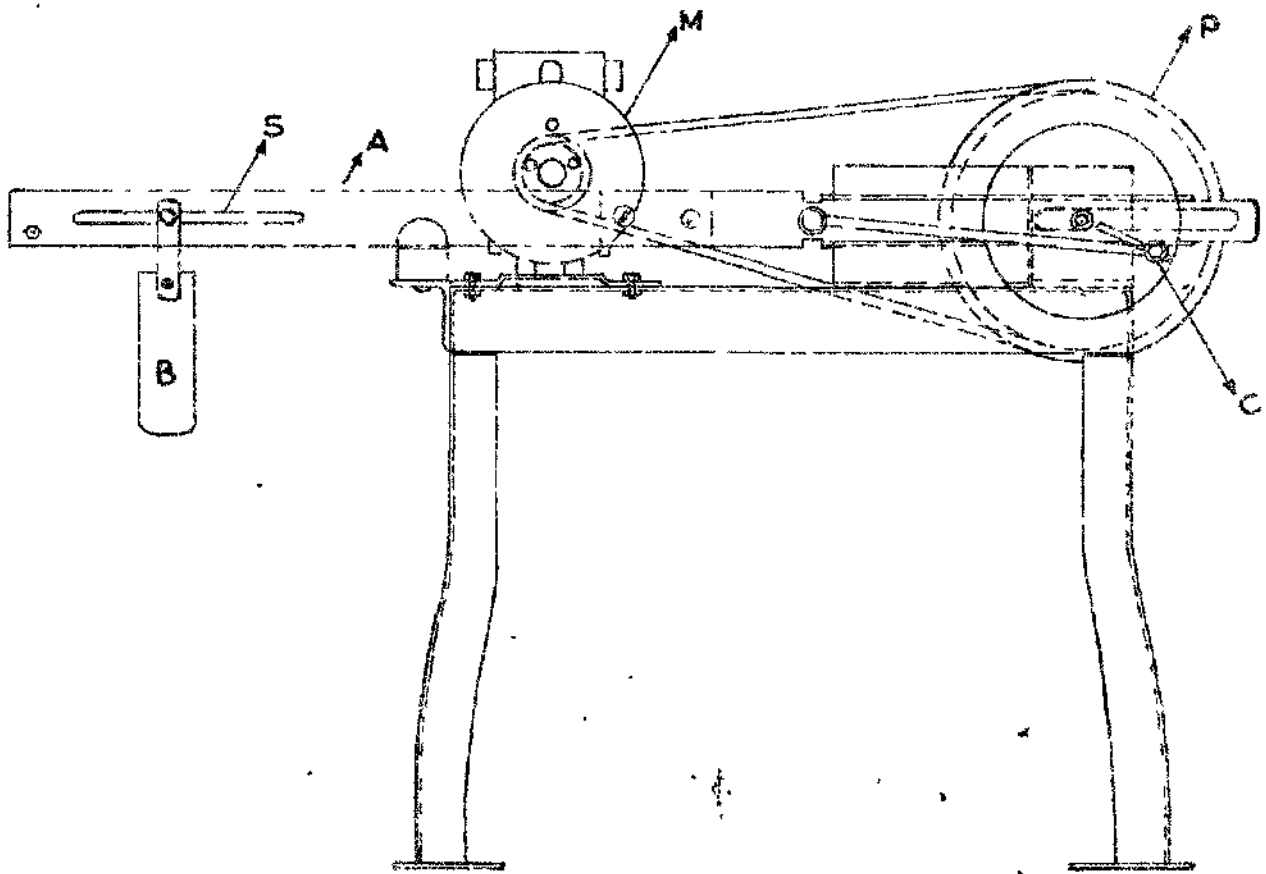


Fig. 1

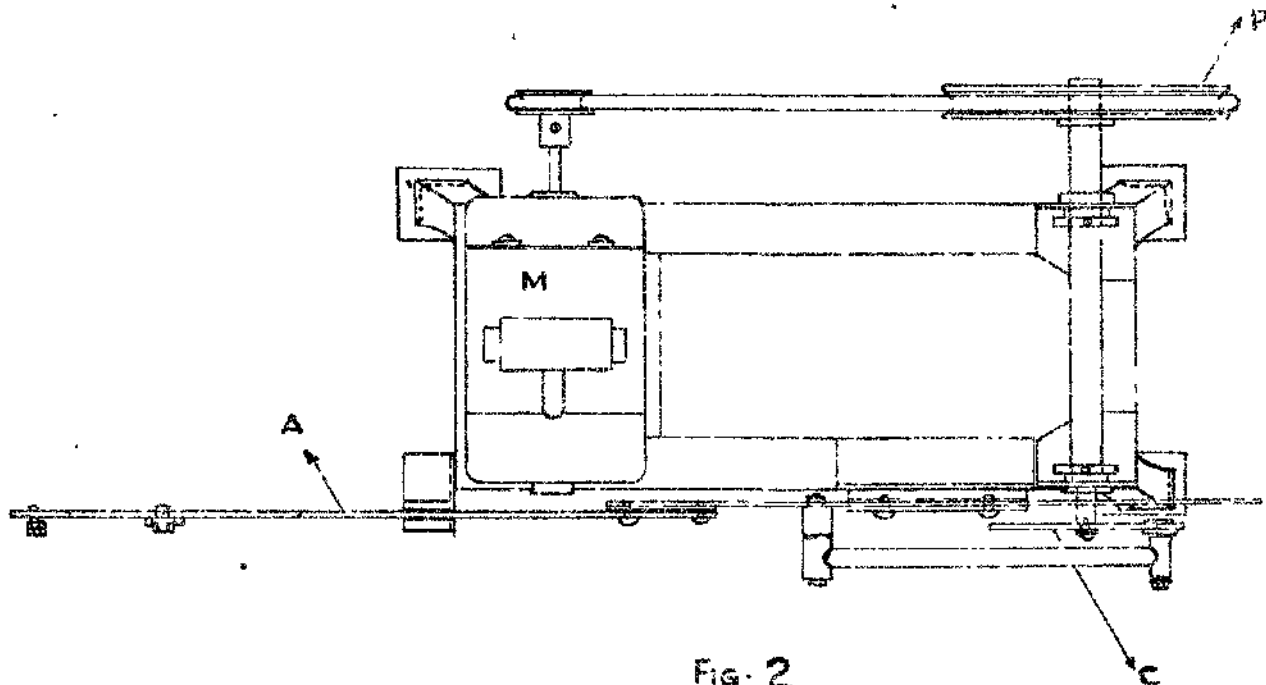


Fig. 2

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