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# PROVISIONAL SPECIFICATION.

## IMPROVEMENTS IN OR RELATING TO LEAD DIOXIDE SEMICONDUCTORS IN THE PREPARATION OF RECTIFIERS.

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, of Central Electrochemical Research Institute, Karaikudi, Madras, India, an Indian citizen

The investigation leading to the invention is briefly recounted here. Lead dioxide is deposited on graphite rod using a bath containing lead nitrate and copper nitrate. The cylindrical rod containing an adherent deposit of lead dioxide is used as one electrode with a platinum gauze as the other electrode surrounding the same in the A. C. electrolysis of 53 per cent. sulphuric acid containing manganese sulphate in solution. It is observed that the surface of lead dioxide is reduced to lead metal and manganous sulphate is oxidised to manganic sulphate at the platinum electrode. This indicated that rectification of A. C. took place and the D. C. component brought about the above electrolytic oxidation of manganous sulphate.

In subsequent experiments, it was observed that the lead dioxide surface could be reduced to lead metal in sulphuric acid of above 40 per cent. strength by passing A. C. as above.

The lead dioxide was deposited on a rotating cylindrical graphite rod and an adherent deposit free from porosity was obtained. On keeping a lead foil on the deposit and pressing the same by means of copper sheets kept on either side and connecting the copper strips and the graphite core to the two A. C. terminals respectively it was found that rectification of A. C took place.

In further experiments carried out, it has been observed that contact on lead dioxide can be made by pressing such mteal foils as aluminium, copper and tin etc., as above and rectification of A. C. obtained.

Similarly, rectification was observed to be better in the case of the rod whose lead dioxide surface had been earlier reduced to metallic lead as stated above. The contacts as well as rectification were found to be better this way.

The rectification obtained was examined by photographing the wave form of the output by means of an oscilloscope.

Lead dioxide was then deposited on nickel sheet and the rectification brought about by such a deposit was also examined. Rectification obtained while reducing the lead dioxide surface in 55 per cent. sulphuric acid was also examined. After the surface was reduced to metallic lead, contact was made as described earlier and the rectification was observed to be better.

Lead dioxide could be deposited on tantalum also and the deposit indicated rectifying action here also on electrolyzing with A. C. in 55 per cent. sulphuric acid, the surface of lead dioxide was reduced to metallic lead almost readily.

Similarly it was found possible to obtain a deposit on stainless steel which could also be given the above treatment so as to be used in rectifiers.

It has further been observed that lead dioxide formed electrolytically by anodic oxidation of lead metal could be successfully used for rectifiers by making contact on the lead dioxide by means of various metal foils described earlier.

### Experiment 1.

Lead dioxide was deposited on a 1 cm diameter graphite rod rotating at 1000 r.p.m. so as to obtain an adherent and smooth deposit free from pinholes etc. A lead foil was wrapped round the same and pressed by means of two copper strips kept on either side and a G-clamp. This was included in the A. C. circuit, graphite forming one electrode and the copper strip the other electrode. Good rectification was observed.

### Experiment 2.

The above rod was kept vertically in the centre of a 100 cc beaker and surrounded by a platinum gauze electrode 55 Per cent. sulphuric acid was taken as electrolyte and graphite and platinum are connected to the terminals, and A. C. of 0.3 amp. was passed, the surface of lead dioxide was reduced to metallic lead. Rectification obtained with this system was observed to be slightly better than in Experiment 1.

### Experiment 3.

The graphite rod with a deposit fo lead dioxide whose surface has been reduced to metallic lead as in Experiment 2, was taken and a lead foil wound on the lead surface and pressed by G-clamp keeping copper strips as in Experiment 1. The rectification obtained was found to be much better than in Experiment 1.

Similar experiments as above were carried out by depositing lead dioxide on nickel sheet. Similar results were obtained

The deposit obtained on tantalum also rectified A. C. to D. C.

### Experiment 4.

Lead dioxide was formed on lead sheet using it as anode in a bath containing ammonium sulphate 135 g/l and sulphuric acid 5 g/l and a trace of nitric acid at room temperature for sufficient time (nearly 24 hours) to give a layer on which a counter electrode (foils of lead, aluminium, copper and tin) was applied. The lead and the counter electrode connected to A. C. terminals respectively indicated rectification of same to D. C.

*Preparation of rectifier.*—(a) Graphite and stainless steel discs of 2 cm diameter and the former of 0.5 cm thick and the latter 1/16" thick, were thoroughly cleaned, degreased and washed. In the case of graphite disc, lead dioxide was deposited from the nitrate bath containing 380 g/l lead nitrate and 18 g/l copper nitrate In the case of stainless steel and other metals, lead dioxide was deposited from a lead sulphamate bath containing 207 g/l lead. After a deposit of about 1 mm thick was formed on the discs, they were removed and then thoroughly washed

The discs were then immersed in 55 per cent. sulphuric acid with the graphite serving as on terminal for A. C. A platinum gauze electrode surrounded the disc and served as the other electrode. A. C. of 0.3 amp. was passed for 5 to 10 minutes when the surface of lead dioxide was reduced to metallic lead. The discs were removed, washed thoroughly and dried. Lead foils are kept on either side of the discs and pressed by keeping copper strips and using a G-clamp Such units have been used to give single phase half-wave rectification as well as full-wave rectification by bridge connection.

(b) A lead disc one inch in diameter with a ¼" hole in the centre was oxidized for nearly 24 hours as in Experiment 4. It was thoroughly washed and dried Two lead foils were kept on either side and pressed together by copper discs which were connected to one terminal. Lead formed the other lead A. C. output from 0-12 volt transformer was connected to the two terminals of the rectifier. A direct current of 0 2 to 0.3 ampere could be drawn through the same continuously

The above experiments are an indication of the possibility of using lead dioxide as a semiconductor for

rectification of A. C. to D. C. The rectification is better when the electrolytically deposited lead dioxide surface is reduced to metallic lead and then used in the preparation of dry rectifiers. The technique adopted for metallising the contact on the semiconductor, lead dioxide is unique and novel.

The following are among the noteworthy features of this invention :

(1) A process wherein lead dioxide electrolytically deposited on graphite, nickel, nickel plated copper, tantalum, stainless steel and monel or electrolytically formed on lead by anodic oxidation of lead metal can be used as a semiconductor in rectifiers.

(2) Lead dioxide is deposited from a bath containing soluble salt of lead such as nitrate, perchlorate, chlorate, acetate and sulphamate to obtain an adherent deposit of the same, free from pinholes and imperfections.

(3) Lead dioxide is formed on lead by anodic oxidation of lead.

(4) The surface of lead dioxide deposited as in (2) is reduced to metallic lead by using it as one electrode in strong acid, preferably in sulphuric acid of strength above 40 per cent. with another electrode, preferably platinum, and passing A. C. for electrolysis

(5) A process as in (3) which could be directly used as an electrolytic rectifier.

(6) Contact on electro-deposited lead dioxide is made by keeping a lead foil and pressing the same

(7) Contact on electro-deposited lead dioxide is made by keeping such metal foils as that of aluminium, copper, silver and tin etc. and pressing the same to serve as the other terminal.

(8) A process as in (4) whereby the metallic lead produced on lead dioxide surface favours formation of good contact on lead dioxide.

(9) A process as in (3) wherein contact on lead dioxide electrolytically formed on lead is made by means of metal foils as those of lead, aluminium, silver and tin.

10. A process wherein graphite, stainless steel, nickel, nickel plated copper tantalum, monel, etc., act as one electrode and lead on lead dioxide, or other metal contacts on lead dioxide as hereinbefore described act as the other electrode in the construction of rectifiers.

The invention includes within its scope a process wherein rectifiers are produced in substantially the same way as hereinbefore described.

R. BHASKAR PAI,

*Patents Officer,*

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

***Dated this 8th day of December 1958.***

# COMPLETE SPECIFICATION.

## IMPROVEMENTS IN OR RELATING TO LEAD DIOXIDE SEMICONDUCTORS IN THE PREPARATION OF RECTIFIERS.

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, OF CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, MADRAS, INDIA, AN INDIAN CITIZEN.

This invention relates to improvements in or relating to lead dioxide semi-conductor in the preparation of rectifiers.

Existing literature does not provide adequate information concerning the use of lead dioxide semi-conductor in the preparation of rectifiers.

The object of the present invention is to develop a process which will enable the use of lead dioxide as a semi-conductor in both electrolytic and dry rectifiers.

The invented process for the preparation of rectifiers by applying a counter-electrode on lead dioxide semiconductor is characterised in that lead dioxide is electrolytically deposited on a metallic or graphite base or lead dioxide is electrolytically formed on lead metal.

Lead dioxide required for the purpose is produced (a) either by anodic deposition of same from a solution containing soluble salts of lead or by (b) electrolytically forming the same by the anodic oxidation of metallic lead.

In the preparation of *dry rectifiers*, lead dioxide is deposited on graphite, stainless steel, tantalum, titanium, nickel or nickel-plated metals as basis materials which themselves act as one of the leads of the rectifier. The counter-electrode on lead dioxide is applied by any of the usual procedures (i) by metal foils being pressed on the same (ii) or by spraying metals on the same or (iii) by reducing the surface of lead dioxide to metallic lead.

In the process where lead metal is oxidized to lead dioxide, lead metal, the basis material itself acts as one terminal of the rectifier. The counter electrode in this case is again applied by either of the first two procedures suggested above.

In the case in which lead dioxide anodically deposited as above is used as an *electrolytic rectifier*, the electrolyte used is sulphuric acid of strength more than 40 per cent. The basis material on which lead dioxide is deposited acts as one terminal. An insoluble anode such as of platinum surrounding the former act as the other terminal, sulphuric acid of suitable strength being the electrolyte, not touching the basis material. When the two terminals are connected to a source of A. C. the surface of lead dioxide is reduced to metallic lead and rectification is observed. This technique also serves as the procedure (iii) enumerated above for preparing the counter-electrode in the preparation of dry rectifiers.

When lead dioxide is used as electrolytic rectifier, it is possible to bring about the oxidation of manganous and cerous sulphates, etc., to manganic and ceric sulphates respectively in solution in the acid used as electrolyte.

A series of examples are given below describing the manner of performing the various steps involved in the preparation of rectifiers and the different ways in which this can be done.

### EXPERIMENT 1.

*Use of electrolytically deposited lead dioxide.*

Lead dioxide was deposited on a 1 cm diameter graphite rod rotating at 1000 r.p.m. so as to obtain an adherent and smooth deposit free from pinholes, etc. A lead foil was wrapped round the same and pressed by means of two copper strips kept on either side and a G-clamp. This was included in the A. C. circuit, graphite forming on terminal and the copper strip the other. Good rectification was observed. Similarly, by spraying aluminium metal on the lead dioxide and using it, gave rectification of A. C. to D. C.

### EXPERIMENT 2.

*Electrolytic Rectifier*

The above rod was kept vertically in the centre of a 100 cc beaker and surrounded by a platinum gauze

electrode. 55 Per cent. sulphuric acid was taken as electrolyte and graphite and platinum are connected to the terminals, and A. C. of 0.3 amp. was passed, the surface of lead dioxide was reduced to metallic lead. Rectification obtained with this system was observed to be slightly better than in Experiment 1.

EXPERIMENT 3.

The graphite rod with a deposit of lead dioxide whose surface has been reduced to metallic lead as in Experiment 2, was taken and a lead foil wound on the lead surface and pressed by G-clamp keeping copper strips as in Experiment 1. The rectification obtained was found to be much better than in Experiment 1.

Experiments carried out as above by depositing lead dioxide on nickel sheet and nickel plated copper and aluminium discs gave similar results.

The lead dioxide deposit obtained on tantalum and titanium also rectified A. C. to D. C. when counter electrodes were applied on the deposit.

EXPERIMENT 4.

*Use of electrolytically formed lead dioxide.*

Lead dioxide was formed on lead sheet using it as anode in a bath containing ammonium sulphate 135 g/l and sulphuric acid 45 g/l and a trace of nitric acid at room temperature for sufficient time (nearly 24 hours) to give a layer on which a counter electrode (foils of silver, aluminium, copper and tin) was applied. The lead and the counter electrode connected to A. C. terminals respectively indicated rectification of same to D. C.

*Preparation of dry rectifier.*—(a) Graphite and stainless steel discs of 2 cm diameter and the former of 0.5 cm thick and the latter 1/16" thick, were thoroughly cleaned, degreased and washed. In the case of graphite disc, lead dioxide was deposited from the nitrate bath containing 380 g/l lead nitrate and 18 g/l copper nitrate. In the case of stainless steel nickel plated and other metals, lead dioxide was deposited from a lead sulphate bath containing 207 g/l lead. After a deposit of about 0.5 to 1 mm thick was formed on the discs, they were removed and then thoroughly washed.

The discs were then immersed in 55 per cent. sulphuric acid with the graphite serving as one terminal for A. C. A platinum gauze electrode surrounded the disc and served as the other electrode. A. C. of 0.3 amp. was passed for 5 to 10 minutes when the surface of lead dioxide was reduced to metallic ead. The discs were removed, washed thoroughly and dried. Lead foils are kept on either side of the discs and pressed by keeping copper strips and using a G-clamp. Such units have been used to give single phase half-wave rectification as well as full-wave rectification by bridge connection

(b) A lead disc one inch in diameter with a ¼" hole in the centre was oxidized for nearly 24 hours as in Experiment 4. It was thoroughly washed and dried. Two tin foils were kept on either side and pressed together by copper discs which were connected to one terminal. Lead formed the other lead. A. C. output from 6-12 volt transformer was connected to the two terminals of the rectifier. A direct current of 0.2 to 0.3 ampere could be drawn through the same continuously.

The above experiments are an indication of the possibility of using lead dioxide as a semi-conductor for rectification of A. C. to D. C. The rectification is better when the electrolytically deposited lead dioxide surface is reduced to metallic lead and then used in the preparation of dry rectifiers. The technique adopted for metallising the contact on the semi-conductor, lead dioxide is unique and novel.

We claim:

1. A process for the preparation of rectifiers by applying a counter-electrode on lead dioxide semi-conductor wherein lead dioxide is electrolytically deposited on a metallic or graphite base or lead dioxide is electrolytically formed on lead metal.

2. A process as claimed in Claim 1 wherein lead dioxide is electrolytically deposited on graphite, nickel, nickel plated metals, titanium, tantalum, stainless steel or monel.

3. A process as claimed in Claim 1 wherein lead dioxide is electrolytically formed on lead by anodic oxidation of lead metal.

4. A process as claimed in Claim 2 wherein lead dioxide is deposited from a bath containing soluble salt of lead such as nitrate, perchlorate, chlorate, acetate and/or sulphamate to obtain an adherent deposit of the same, free from pinholes and imperfections.

5. A process as claimed in Claim 1 or 2 wherein the surface of lead dioxide deposited is reduced to metallic lead by using it as one electrode in strong acid, preferably in sulphuric acid of strength above 40 per cent with another electrode, preferably platinum, and passing A. C. for electrolysis, so that by electrolytic rectification metallic lead formed serves as a counter-electrode.

6. A process as claimed in any of the preceding claims wherein the counter-electrode is applied on electro-deposited and/or electrolytically formed) lead dioxide by keeping metal foils on the lead dioxide and pressing the same or by spraying metals on the lead dioxide.

7. A process as claimed in Claim 6 wherein metal foils of lead, aluminium, copper, silver or tin are used.

8. A process for the preparation of rectifiers substantially as hereinbefore described.

9. Rectifiers using lead dioxide as a semi-conductor whenever prepared according to a process substantially as hereinbefore described

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*Dated this 7th day of September* 1959.

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