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Specification No. 101712. Application No. 101712, dated 25th September 1965. Complete Specification left on 20th June 1966. (Application accepted 20th June 1967.)

Index at acceptance—70C4[LVIII(5)], 130G[XXXIII(7)].

IMPROVEMENTS IN OR RELATING TO RECOVERY OF ZINC FROM BY-PRODUCT ZINC COMPOUND.  
**PROVISIONAL SPECIFICATION.**

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAJF MARG, 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, Scientist and PENNAGARAM VYASA RAO VASUDEVA RAO, Scientist, both Indians and both of Central Electrochemical Research Institute, Karaikudi-3, India.

This invention relates to improvements in or relating to recovery of zinc from by-product zinc oxide|hydroxide|or carbonate from hydrosulphite and other chemical industries and by-product zinc oxide from paint and galvanizing industry by the direct reduction technique.

Hitherto it has been proposed to bring the zinc oxide|hydroxide into solution with appropriate alkali or acid and electrolyse the aqueous solution for recovering the zinc in powder or plate form depending on the conditions of electrolysis.

This is open to objection that (a) the quantity of alkali or acid required is twice or more than the stoichiometric ratio to completely dissolve the oxide|hydroxide of zinc, thereby upsetting the other conditions of electrolysis; (b) large volumes of electrolyte has to be handled and unit operations such as dissolution, filtration etc., are necessary; (c) the conditions of electrolysis are to be maintained carefully to obtain product of specific characteristics; (d) certain types of zinc oxide|hydroxide stored for a long duration are not readily soluble in alkali and heating is necessary to obtain the same in the solution form.

The object of this invention is to obviate these disadvantages by the method of "Direct reduction technique" by which the oxide|hydroxide etc., is used as a solid depolariser kept on a suitable sheet-metal cathode and a suitable anode in alkaline medium and passing current, the sediment of zinc oxide|hydroxide directly getting reduced to zinc powder. This method thus avoids the necessity of the zinc compound being taken into solution and so the connected unit operations. The running of the cell requires minimum of maintenance and technical knowledge. Bipolar cells can be used for bringing about the reduction and saving on floor space. The type of product obtained depends mainly on the type of starting material and hence can be controlled by controlling the starting material.

To these ends the invention broadly consists in keeping the solid zinc oxide|hydroxide as a bed at the bottom of a mild steel, stainless steel, nickel or any other suitable nickel plated metal container which is not attacked by alkali, and using an anode over the bed so disposed that there is a uniform current distribution and the distance so adjusted that the voltage of the cell will be minimum. Sodium hydroxide solution of appropriate strength is used as the electrolyte. The description of the cell is as follows:

(a) A rectangular or a circular cell made of 1/8" mild steel sheet is used. The anode is mounted on an insulating strip of PVC, perspex, cement board or glazed ceramic material not attacked by alkali. The connecting strips of the anode and the leads from the cathode are so designed that it has necessary current carrying capacity. The zinc oxide|hydroxide to be reduced is evenly spread on the bottom of the cell. The rest of the portions of the cell are stopped off with an epoxy resin such as Araldite or any other suitable substance, to avoid loss of current efficiency due to hydrogen evolution. The sodium hydroxide solution is pumped in without disturbing the bed of the solid substance. This is achieved by first mounting the perforated anode assembly and then allowing the sodium hydroxide solution to pass through the same. The alkali level is so adjusted that it covers the anode completely and is about 5 to 7.5 cm from the cell bottom. The depth of the oxide bed, the level of the electrolyte in the cell and the anode assembly are all variables, depending on the experimental conditions.

(b) Alternatively, a cell is made of concrete of proper wall thickness, into which a suitable metal sheet of mild

steel, stainless steel, nickel or similar metal not attacked by alkali is inserted before the concrete is set, so that the sheet serves as the bottom of the cell. This tank is used in the place of the mild steel tank described in the foregoing para and this arrangement avoids the stopping off of the sides of the electrolytic cell. The anode assembly and the rest of the conditions remain the same as for the mild steel cell.

The following typical examples are given to illustrate the invention.

**EXAMPLE 1**

In an experiment with a smaller cell similar to one described above, 475 g of zinc oxide obtained from a chemical plant was reduced. The zinc oxide bed was 1.5 cm thick and 20% alkali was used as electrolyte. The reduction was carried out for 18 hours at 20 amp (5 amp/dm<sup>2</sup>) over which the average voltage was 2.8 V. 380 g of zinc powder was obtained from the cell after proper processing etc. The current efficiency was about 90% and conversion efficiency was 100%. The zinc content of the powder was 93% and total zinc was over 96%.

**EXAMPLE 2**

In a cell designed for large scale operation, reduction of 25 kg of zinc oxide was carried out. 300 amps were passed for 72 hours and the cell voltage was 3.0 V (average). The height of the oxide bed was 1.0 cm and 20% alkali was used as the electrolyte. The cell was run for about 72 hours continuously. The current efficiency was 85% conversion was complete.

*Description of Bipolar Cells:*

The cells described in 3a are stacked one over the other in such a way that the bottom of the top cell immersed in the electrolyte of the lower cell acts as the anode, and the interior acts as the cathode; thus setting up a bipolar arrangement of the cells. The anode is disposed as described in 3a at the topmost cell and the bottom most cell is connected as the cathode.

**EXAMPLE 3**

In an experiment with the above arrangement of bipolar cell for reduction of zinc oxide, four cells were arranged in the manner described above, the bottom most cell being connected as the cathode. The total voltage of the system was 10 volts (average) for a current density of 10 amp/dm<sup>2</sup>. Each cell contained 0.5 kg of material and the reduction was carried out for 40 hours. Complete reduction with a current efficiency of 80-85% was achieved. The total weight of zinc powder obtained was 1.35 kg with a recovery efficiency of 96.5%, the rest being accounted for in the electrolyte.

*Processing of the powder:*

After reduction is over, the powder is scooped out of the cell, washed well, centrifuged and dried after suitably stabilising the powder.

When the powder is required to be used in the wet form for the process, for example in a chemical reduction plant, such as for hydrosulphite manufacture, the powder from the wash tank, is directly transferred to the reaction tank.

*Starting material:*

When the impurities contained in the zinc oxide|hydroxide do not interfere with the application of the powder, the starting material need not be given any pre-treatment or purification.

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Where the impurities in the zinc oxide|hydroxide are harmful for the future application of the zinc powder, the oxide or hydroxide is given a roasting treatment to remove the volatile impurities and then taken for reduction.

The following are the main advantages of the invention :

(1) The step of bringing the zinc oxide|hydroxide into solution for electrolysis is eliminated which in turn eliminates handling of large volume of solutions and unit operations like filtration etc.

(2) Requires minimum maintenance of variable parameters such as current density, concentration etc.

(3) The product can be straightaway used in the processes where wet zinc powder or zinc powder contaminated with sodium hydroxide is not objectionable. This eliminates the intermediate steps of washing, centrifuging, stabilizing, drying, packing etc.

(4) The process is in a way cyclic with reference to zinc powder if (3) above is adopted except for make up zinc powder required for handling losses.

(5) The process is unique in that zinc powder required for chemical reduction can be produced on the spot.

(6) Bipolar cells can be used, leading to savings in energy, busbar and floorspace expenditure.

R. BHASKAR PAI,

Scientist,

COUNCIL OF SCIENTIST AND INDUSTRIAL RESEARCH.

Dated this 28th day of August 1965.

## COMPLETE SPECIFICATION.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJ MARG, 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, Scientist and PENNAGARAM VYASARAO VASUDEVA RAO, Scientist, both of Central Electrochemical Research Institute, Karaikudi-3, India, both Indian citizens.

This invention relates to improvements in or relating to recovery of zinc from byproduct zinc compounds such as zinc oxide|hydroxide or carbonate from hydrosulphite and other chemical industries and byproduct zinc oxide from paint and galvanizing industry by the direct reduction technique.

### *Prior knowledge :*

Hitherto it has been the practice to bring the zinc oxide|hydroxide|carbonate into solution with appropriate alkali or acid and electrolyse the aqueous solution for recovering the zinc in powder or plate form, depending on the conditions of electrolysis.

### *Drawbacks connected with hitherto known processes|devices :*

The disadvantages in the older processes are as follows :

(a) The quantity of alkali or acid required is twice or more than the stoichiometric ratio to completely dissolve the oxide|hydroxide|carbonate of zinc, thereby upsetting the other conditions of electrolysis.

(b) Large volumes of electrolyte has to be handled and a number of unit operations such as dissolution, filtration etc., are necessary.

(c) The conditions of electrolysis are to be maintained carefully to obtain product of specific characteristics.

(d) Certain types of zinc oxide|hydroxide stored for a long duration are not readily soluble in alkali and heating is necessary to obtain the same in the solution form.

### *Main object of the invention :*

The object of the present invention is to obviate these disadvantages by the method of DIRECT REDUCTION TECHNIQUE in which the oxide|hydroxide|carbonate kept on a suitable sheet metal cathode and is used as a solid depolarizer and on passing the current with a suitable anode in an alkaline medium, the sediment of zinc oxide|hydroxide directly gets reduced to give zinc powder.

### *The main finding upderlying the invention:*

The solid zinc compound is kept as a sediment as the bottom of the cell and the cell is made of the cathode. Sodium hydroxide solution serves as the electrolyte and as the current is passed, the zinc oxide|hydroxide gets reduced to the zinc powder.

### *The new result :*

This process of direct reduction offers certain advantages viz., (a) this eliminates the intermediate steps of bringing the

zinc compound into solution and electrolysing the same subsequently; (b) this avoids handling of large volumes of solution; (c) the running of the cell requires minimum of maintenance and technical knowledge. (d) Bipolar cells can be used for bringing about the reduction and saving of floor space. (e) The type of product obtained depends mainly on the type of starting material and hence can be controlled by controlling the starting material.

According to the present invention the process for the recovery of zinc from byproduct zinc compounds consists in subjecting the said compounds to direct electrochemical reduction by keeping them as a sediment on a metal substrate or on the bottom of the container which serves as the cathode in an alkaline electrolyte employing a suitable metal such as mild steel, nickel plated mild steel, nickel or stainless steel in the form of wire mesh or perforated sheet as anode and keeping the anode immersed in the electrolyte.

The zinc compound may consist of solid zinc oxide or zinc hydroxide or zinc carbonate obtained as a byproduct during the production of hydrosulphite and/or other organic or inorganic chemicals, using zinc metal powder in the process, or zinc oxide obtained from paint and galvanizing industries.

An aqueous solution of alkali of 10% to 30% strength, preferably 20% of sodium hydroxide, is used as electrolyte at a temperature not exceeding 50°C, preferably at room temperature  $30 \pm 2^\circ\text{C}$ , using a current density upto 30 amp/dm<sup>2</sup> but preferably 10 amp/dm<sup>2</sup>, employing mild steel, nickel or nickel plated mild steel as the cathode.

If the zinc compound used in the process of reduction contains an impurity insoluble in alkali and accrued from the process from which the zinc compound is obtained as a byproduct then the zinc powder obtained will contain the same impurity.

The zinc powder is obtained in the wet condition and is used straightaway in organic or inorganic reduction processes such as production of hydrazobenzene, phenylhydroxylamine and of hydrosulphite.

The apparatus for carrying out the process which comprises a group of convenient number of cells for example four cells, stacked one over the other mounted on a frame in such a way that the bottom of the top cell immersed in the electrolyte of the lower cell acts as the anode and the interior acts as the cathode, thus setting up a bipolar arrangement of the cells; the bottom most cell is connected as the cathode and the anode is disposed over the top most cell.

The alkaline electrolyte is used continuously by making up the loss during processing by addition of fresh electrolyte.

Thus, the present process for the recovery of zinc from byproduct zinc oxide|hydroxide|carbonate from hydrosulphite

and other chemical industries and byproduct zinc oxide from paint and galvanizing industry involves the direct reduction of zinc oxide|hydroxide|carbonate kept as a sediment on a cathode wherein the zinc can be recovered from these by-products without bringing the same into solution for subsequent electrolysis:

The conversion efficiency is nearly 100% with a current efficiency of 85-90%.

*Detailed description with reference to accompanying drawings:*

In this process, zinc is recovered as zinc powder by direct electrochemical reduction of zinc oxide|hydroxide|carbonate obtained as byproduct in a suitable cell arrangement using an alkaline electrolyte. The cell (No. 1 in Figs. 1 and 2) can be made of mild steel, stainless steel, nickel or any other suitable nickel plated metal container which is not attacked by alkali. The description of the cell is as follows:

(a) A rectangular or circular cell made of 1/8" mild steel sheet is used. The anode assembly (No. 2 in Figs. 1 and 2) consists of a mild steel, nickel plated mild steel, nickel or stainless steel mesh and is mounted on an insulating strip (No. 3 in Fig. 1) of PVC, perspex, cement board or glazed ceramic material, not attacked by alkali. The anode is mounted in such a way as to facilitate uniform current distribution and the distance between the anode and the cathode is so adjusted that the cell voltage will be minimum. The cell itself is used as the cathode. The connecting strips of the anode and the leads from the cathode are so designed that it has the required current carrying capacity. The zinc compound (No. 4 in Figs. 1 and 2) to be reduced is evenly spread on the bottom of the cell. The sides of the cell are stopped off with an epoxy resin such as Araldite or any other suitable substance to avoid loss of current efficiency due to hydrogen evolution. The sodium hydroxide solution is pumped in without disturbing the bed of the solid substance. The alkali level is so adjusted that it covers the anode completely and is about 5 to 7.5 cm from the cell bottom. The depth of the oxide bed, the level of electrolyte in the cell and the anode assembly are all variables depending on the experimental conditions.

(b) Alternatively, a cell is made of concrete of proper wall thickness, into which a suitable metal sheet of mild steel, nickel or similar metal not attacked by alkali is inserted before the concrete is set, so that the sheet serves as the bottom of the cell. This tank is used in the place of the mild steel tank described in the foregoing para and this arrangement avoids the stopping off the sides of the electrolytic cell. The anode assembly and the rest of the conditions remain the same as for the mild steel cell.

Finely powdered zinc compound is used and a current density of 10 amp/dm<sup>2</sup> is employed. 20% sodium hydroxide serves as the electrolyte and 10% excess current over that is theoretically required for the amount of zinc compound taken for reduction, was passed. At the end of the reduction, the powder was removed from the cell, washed free from alkali and stabilised and finally dried.

(c) *Description of Bipolar cells:* The cells described under 12 (a) are stacked one over the other in such a way that the bottom of the top cell immersed in the electrolyte of the lower cell acts as the anode, and the interior acts as the cathode, thus setting up a bipolar arrangement of the cells. The cell arrangement is presented in Fig. 2. The cells are stacked one over the other and are fitted in position in an insulating frame (No. 3 in Fig. 2). The bottom most cell is connected as the cathode and the anode is disposed over the top most cell as shown in Fig. 2. As an example, the arrangement consisting of four such cells is shown in Fig. 2.

*Typical Examples:*

**EXAMPLE 1**

In an experiment with a smaller cell similar to one described in 12 (a), 475 g of zinc oxide obtained from a chemical plant was reduced. The oxide bed was 1.5 cm thick and 20% alkali was used as electrolyte. The reduction was carried out for 18 hours at 20 amps (5 amp/dm<sup>2</sup>) over which the average voltage was 2.8 V. 350 g of zinc powder was obtained after proper processing etc. The current efficiency was about 90% and conversion efficiency was 100%. The zinc content of the powder was 83-86% and total zinc was over 96%.

**EXAMPLE 2**

In a cell designed for large scale operation, 25 kg of zinc oxide was reduced. 300 amps were passed for 72 hours and the cell voltage was 3.0 V (average). The height of the oxide bed was 1.0 cm and 20% alkali was used as the electrolyte. The cell was run for about 72 hours continuously and the current efficiency was 85% and conversion was complete.

**EXAMPLE 3**

In an experiment with the arrangement of bipolar cells as described in 12(c), four cells were arranged in the manner described under 12(c), the bottom most cell being connected as the cathode. The total voltage of the system was 10 V (average for a current density of 10 amp/dm<sup>2</sup>). Each cell contained 0.5 kg of the material and the reduction was carried out for 40 hours. Complete reduction with a current efficiency of 80-85% was achieved. The total weight of zinc powder obtained was 1.35 kg with a recovery efficiency of 96.5%, the rest being accounted in the electrolyte.

*Main advantages:*

The following are the main advantages of the invention:

(a) The step of bringing the zinc oxide|hydroxide into solution for electrolysis is eliminated which in turn eliminates handling of large volumes of solutions and unit operations like filtration etc.

(b) Requires minimum maintenance of variable parameters such as current density, concentration etc.

(c) The product can be straightaway used in the reduction processes where wet zinc powder or zinc powder contaminated with sodium hydroxide is not objectionable. This eliminates the intermediate steps of washing, centrifuging, stabilizing, drying, classifying and packing and also avoids possible oxidation of the powder during these operations.

(d) The process is in a way cyclic with reference to zinc powder if (c) above is adopted except for make up zinc powder required for handling losses.

(e) The process is unique in that zinc powder required for chemical reduction processes can be produced on the spot.

(f) Bipolar cells can be used, leading to savings in energy, busbar and floor space expenditure.

(g) The type of the product obtained depends on the type of starting material and hence can be controlled by controlling the starting material.

*Summary:*

This invention relates to the recovery of zinc in the form of powder from byproduct zinc compounds obtained from hydrosulphite and other chemical industries, paint and galvanizing industries by direct reduction technique. This process of direct reduction of the byproduct zinc compounds to zinc powder in an alkaline medium has a number of advantages one of which is the elimination of the step of bringing the compound into solution and subsequent electrolysis of the solution. Mild steel, stainless steel, nickel or nickel plated mild steel container serves as the cathode and a mild steel, stainless steel, nickel or nickel plated mild steel mesh suitably disposed serves as the anode. The anode assembly is mounted on an insulating frame. The material to be reduced is kept as a sediment at the bottom of the cell. Sodium hydroxide solution is used as the electrolyte. As current is passed, the zinc compound gets reduced to the zinc powder gradually. After the reduction is over, the zinc powder is taken out from the cell, washed well, centrifuged and dried after suitably stabilising the powder. The conversion efficiency is 100% with a current efficiency of 85-90%. When the powder is required to be used in the wet form, for the process, for example, in a chemical reduction plant such as for hydrosulphite manufacture, the powder from the wash tank can be directly transferred to the reaction tank. Since the quality of the powder obtained depends much on the type of starting material, the type of powder can be controlled by controlling the starting material itself. When the impurities present in the zinc oxide|hydroxide do not interfere with the application of the powder, the starting material need not be given any pretreatment or purification. If the impurities present are harmful for the future application of the zinc powder obtained, then a roasting treatment may be given to remove volatile and other impurities from the material. Bipolar cells can be used leading to savings in energy and floor space.

We claim :

1. A process for the recovery of zinc from byproduct zinc compounds which consists in subjecting the said compounds to direct electrochemical reduction by keeping them as a sediment on a metal substrate or on the bottom of the container which serves as the cathode in an alkaline electrolyte employing a suitable metal such as mild steel, nickel plated mild steel, nickel or stainless steel in the form of wire mesh or perforated sheet as anode and keeping the anode immersed in the electrolyte.

2. A process as claimed in Claim 1 wherein the zinc compound consists of solid zinc oxide or zinc hydroxide or zinc carbonate obtained as a byproduct during the production of hydrosulphite and/or other organic or inorganic chemicals, using zinc metal powder in the process, or zinc oxide obtained from paint and galvanizing industries.

3. A process as claimed in Claim 1 or 2 wherein an aqueous solution of alkali of 10% to 30% strength, preferably 20% of sodium hydroxide, is used as electrolyte at a temperature not exceeding 50°C, preferably at room temperature  $30 \pm 2^\circ\text{C}$ , using a current density upto 30 amp/dm<sup>2</sup> but

preferably 10 amp/dm<sup>2</sup>, employing mild steel, nickel or nickel plated mild steel as the cathode.

4. A process as claimed in any of the preceding claims wherein the zinc is obtained in the wet condition and is used straightaway in organic or inorganic reduction processes such as production of hydrazobenzene, phenylhydroxylamine, and of hydrosulphite.

5. A process as claimed in any of the preceding claims wherein fresh alkaline electrolyte is added during processing.

6. A process for the recovery of zinc from solid zinc oxide or zinc hydroxide or zinc carbonate substantially as hereinbefore described.

R. BHASKAR PAI,

*Patents Officer,*

COUNCIL OF SCIENTIST AND INDUSTRIAL  
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*Dated this 14th day of June 1966.*

Nº 101712

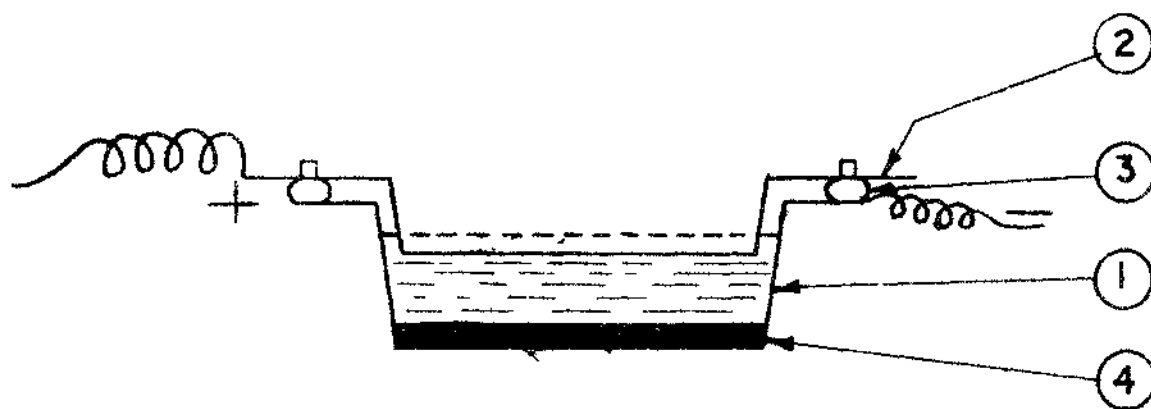


FIG. 1

*R. B. Pai*  
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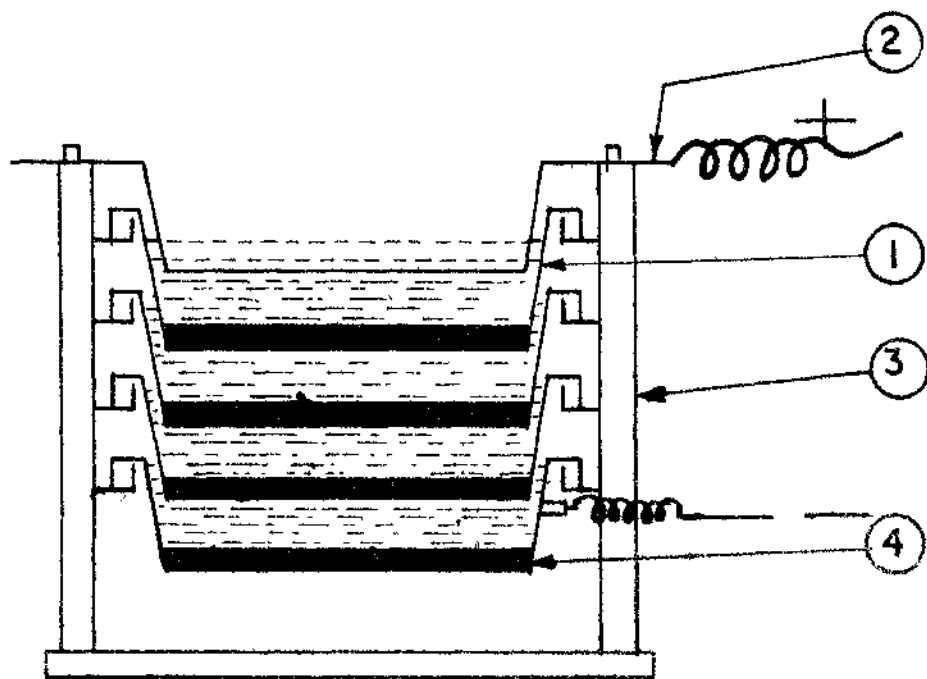


FIG. 2

*R. B. P. A. I.*  
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PATENTS OFFICER,  
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