

Specification No. 69864, Application No. 69864, dated 24th June 1957. [Complete Specification left on 22nd April 1958.] (Application Accepted 19th March 1959.)

PROVISIONAL SPECIFICATION.

IMPROVEMENTS RELATING TO THE ELECTROLYTIC PREPARATION OF SALICYLALDEHYDE.

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 BIMAN BIHARI DEY, BOTH OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, BOTH INDIANS.

The electrolytic preparation of salicylaldehyde developed in this Institute has been substantially described in Indian Patent No. 52631. The present work refers to further improvements effected in the process by using amalgamated rotating cathodes.

The present invention for the electrolytic preparation of salicylaldehyde consists in the stage-wise addition of a solution of salicylic acid and sodium sulphite whereby sodium salicylate and sodium bisulphite are formed *in situ*, to the catholyte containing boric acid and sodium sulphate, using a rotating cylindrical amalgamated cathode and which is characterised in that a temperature not exceeding 25°C. is maintained and a current density range of 2 to 15 amp/dm² is used keeping a critical bath pH range of 5.4 to 6.0, but preferably 5.7. It is further characterised in that the catholyte is neutralised with sulphuric acid at the end of the electrolysis, the sulphur dioxide recovered as sodium sulphite and the sodium sulphate and the unreduced salicylic acid are also recovered, so that the boric acid is repeatedly used for further reductions. The process becomes economical by these steps and a material yield of 65 to 70 per cent. of salicylaldehyde is obtained at a current efficiency of 50 to 55 per cent.

The full details of the invention are given step by step in the following paragraphs.

Details of electrolysis:

Sodium sulphate and boric acid are taken in the catholyte. Salicylic acid and sodium sulphite in aqueous solution are added stagewise during the course of electrolysis. The pH is maintained at 5.4 to 5.7 and not exceeding 6 by the addition of sulphuric acid to the catholyte. 20 per cent. sulphuric acid is used as anolyte. Lead is the anode and a copper cylindrical amalgamated rotating cathode is used so as to have a peripheral velocity of 176 to 235 metres per minute. A cathodic current density of 2 to 15 amp/dm², but preferably about 12 amp/dm² is used and electrolysis carried out for the theoretical period of time at a temperature not exceeding 25°C. When the reductions were carried out in this way, a current efficiency of 52 to 55 per cent. was obtained on a small scale and about 50 per cent. on a large scale.

Recovery of Products:

Attempts have now been made to account for the unreduced salicylic acid so that a material yield of 65 to 70 per cent. of salicylaldehyde has been obtained. After the electrolysis is over, the electrolyte is neutralised with sulphuric acid and steam-distilled. The salicylaldehyde is obtained as an oily layer. The sulphur dioxide evolved is absorbed in soda ash or sodium hydroxide in order to recover the same and the sodium sulphite obtained reused.

The liquor left after steam-distillation on cooling gives a layer of tar from which by reaction with sodium bicarbonate solution a certain amount of salicylic acid is recovered. From the aqueous portion, salicylic acid is recovered by extraction with ether. The salicylic acid thus recovered accounts for about 25 per cent. of the salicylic acid started with. 50 per cent. of the salicylic acid is accounted for as salicylaldehyde. Some amount of a product insoluble in sodium bicarbonate but soluble in alkali is also obtained, whose identity has not been established.

The salt separated is filtered off in the hot state and washed. On cooling boric acid separates out and can be filtered, washed and obtained in a pure condition. In this way, nearly 80 per cent. could be easily recovered and the remaining solution could be reused on making up the electrolyte again. In this way boric acid and sodium sulphate could be reused obtaining sodium sulphate as a bye-product. Alternately, the excess sodium sulphate formed only is separated, so that with the original sodium sulphate in solution, it can be used for further reductions along with the boric acid already present.

Anolyte acid:

20 per cent. sulphuric acid is used as anolyte and a highly porous alumic variety diaphragm helped in the maintenance of strength of acid constant. The sulphuric acid anolyte can be used over and over.

Diaphragm material:

Alumic variety highly porous diaphragm or diaphragm made of collodion serve the purpose very well.

EXAMPLE 1.

20 g. sodium sulphate, 15 g. boric acid in 140 cc. water is taken as catholyte. 14 g. sodium sulphite and 13.8 g. salicylic acid in 45 cc. water are added in 7 cc. lots every 5 minutes. An amalgamated copper cylinder (0.5 dm² area) is used as cathode. 60 cc. of 20 per cent. H₂SO₄ is used as anolyte in a porous pot (medium porosity). A current of 6 amp. is passed for theoretical time at a temperature of 12°-16°C. Nearly 10-13 cc. of 12N H₂SO₄ is added to catholyte during electrolysis to maintain the pH at 5.7 to 6.0. The catholyte is neutralised with 6 cc. of concentrated H₂SO₄ and steam-distilled to recover the salicylaldehyde. 5.6 cc. was obtained accounting for 52.8 per cent. current efficiency.

EXAMPLE 2.

Using collodion diaphragm and repeating the above experiment only about 5 to 6 cc. of 12 N sulphuric acid had to be added in order to maintain the pH. The yield of salicylaldehyde was 5.6 cc. 52.8 per cent.

Large scale Laboratory Experiment:

The cell set up had a capacity of half a pound of salicylaldehyde in 3 hours or 4 lbs. per day of 24 hours and is shown in sheet one as Figure 1 and Figure 2 (sectional and top views respectively) of the accompanying drawings. The cell container H is of hard rubber. Two alumic variety highly porous cylindrical diaphragms D, D are kept on either side of the rotating cylindrical cathode C. The porous pots are resting on perspex tripods T, T. Two lead cooling coils F pass through openings E, in the wooden lid W. Two cylindrical lead anodes A, A are kept inside the porous pots. The cathode is fabricated from 1/16" thick copper plate by making it cylindrical and welding the edge. A wooden core is used and the ends waxed. A 3/8" copper rod is fitted to the top and connection from this to the copper sheet is made so that two brushes B, B make contact on this rod for the cathode. A glass guide G clamped tightly served to give smooth rotation. A 1/16th H.P. motor with a variac served to control the

The cylindrical cathode 3" diameter was rotated at 800 to 1000 r.p.m. 800 g. of sodium sulphate dissolved to give 5200 cc. solution was used. 600 g. boric acid was added. 552 g. salicylic acid and 560 g. of sodium sulphite are dissolved in 1400 cc. water so that nearly 2 litres of solution are obtained. A current of 70-72 amp. are passed and 135 cc. of the above are added once in 10 minutes. The pH maintained at 5.7 to 6.0 by the addition during electrolysis of nearly 150 cc. of 12N sulphuric acid. 700 cc. of 20 per cent. H₂SO₄ in each porous pot was the anolyte and this was increased to one litre in each during electrolysis. Temperature was 15°-18°C. Cell voltage was 14 to 15 volts.

Isolation products :

240 cc. concentrated sulphuric acid was used for neutralising the catholyte and steam-distilled to obtain 244 g. salicylaldehyde (current efficiency, 50 per cent.). 136 g. salicylic acid was also recovered (25 per cent. nearly). The material yield works up nearly to 75 per cent. The energy consumption is 6 k.w.h.r. (D.C.)/lb. of salicylaldehyde. The sulphurdioxide evolved was absorbed in soda ash and nearly 60 per cent. recovered.

The strength of sulphuric acid in the anolyte remained 20 per cent.

The following are among the noteworthy features of the process.

1. A process for the preparation of salicylaldehyde which consists in the electrolytic reduction of salicylic acid using sodium sulphate as electrolyte in the presence of boric acid and wherein a critical pH range, 5.4 to 6.0 is maintained, preferably at 5.7 at a temperature not exceeding 25°C. and using a c.d. range of 2 to 15 amp/dm².

2. A process as in 1 wherein for reducing 13.8 g. of salicylic acid, 20 g. of sodium sulphate and 15 g. boric acid are used in catholyte while using 20 per cent. sulphuric acid as anolyte.

3. A process as in 2 wherein sodium sulphite and salicylic acid are reacted in aqueous solution so as to produce sodium salicylate and sodium bisulphite *in situ* whereby the latter fixes the aldehyde formed.

4. A process whereby the solution of sodium salicylate and sodium sulphite obtained as in 3 is added in stages during reduction and wherein the pH is maintained during electrolysis by the addition of sulphuric acid to the catholyte.

5. A process as above wherein a highly porous alumic diaphragm or a collodion diaphragm is used as anode chamber.

6. A process as above wherein a cylindrical amalgamated rotating cathode is employed so as to have 175 to 225 metres/minute of cathode peripheral velocity.

7. A process whereby the salicylaldehyde is obtained by neutralisation of catholyte with sulphuric acid and steam-distilling and the sulphurdioxide recovered as sodium sulphite.

8. A process as above wherein the unreduced salicylic acid is recovered from the aqueous portion left after steam-distillation by solvent extraction and from the resin by treatment with sodium bicarbonate solution.

9. A process whereby the sodium sulphate is recovered from the solvent extracted solution by evaporation to the point of separation of the same and filtering hot.

10. A process as described in 9, whereby the boric acid is recovered by cooling the filtrate obtained by the above step.

11. Salicylaldehyde prepared according to a process substantially as herein before described and the various raw materials reused as described herein before so as to obtain a current efficiency of 50 to 55 per cent. and a material yield of nearly 65 to 70 per cent. salicylaldehyde.

R. BHASKAR PAI.

Patents Officer,

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

Dated this 20th day of June 1957.

COMPLETE SPECIFICATION.

IMPROVEMENTS RELATING TO THE ELECTROLYTIC PREPARATION OF SALICYLALDEHYDE.

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 BIMAN BIHARI DEY, BOTH OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, BOTH INDIAN CITIZENS.

The electrolytic preparation of salicylaldehyde developed in the Central Electrochemical Research Institute, Karaikudi has been substantially described in Indian Patent No. 52631. The present work refers to further improvements effected in the process by using amalgamated rotating cathodes.

The invented process for the preparation of salicylaldehyde consists in the electrolytic reduction of salicylic acid using sodium sulphate or sodium chloride as electrolyte in the presence of boric acid and wherein a critical pH range, 5.4 to 6.0 is maintained, preferably at 5.7 at a temperature not exceeding 25°C. and using a current density range of 2 to 15 amp/dm² and wherein an aqueous solution of salicylic acid and sodium sulphite (resulting in the formation *in situ* of sodium salicylate and sodium bisulphite in aqueous solution) is added to the catholyte.

The process consists of the following steps :—

1. Sodium salicylate and sodium bisulphite are formed *in situ*, in solution by mixing salicylic acid and sodium sulphite.

acid and sodium sulphate or sodium chloride during electrolysis.

3. Reduction is carried out at a rotating amalgamated cylindrical cathode at a temperature not exceeding 25°C. using a current density range of 2 to 15 amp/dm² keeping a critical catholyte pH range of 5.4 to 6 but preferably 5.7.
4. Aldehyde is separated after electrolysis by neutralizing the catholyte with sulphuric acid or hydrochloric acid and steam distilling.
5. The sulphur dioxide evolved during steam distillation is recovered as sodium sulphite by bubbling the same into soda ash or alkali.
6. Unreduced salicylic acid is recovered by solvent extraction of the catholyte which has been steam distilled as in paragraph 4 above.
7. Sodium sulphate or sodium chloride is recovered by concentration of the electrolyte after solvent extraction and filtering hot.
8. Boric acid is recovered by cooling the hot filtrate.

The process thus

nor specified in the previous patent No. 52631. Further, steps 1 to 3 which relate to the electrolysis and the preparation of sodium bisulphite and sodium salicylate in solution are an improvement over what has been described in the earlier patent. Steps 4 onwards describe the isolation of the aldehyde and the starting chemicals which are to be reused and which definitely is an improvement making the process more economical.

The full details of the invention are given step by step in the following paragraphs.

Details of electrolysis :

Sodium sulphate or sodium chloride and boric acid are taken in the catholyte. Salicylic acid and sodium sulphite in aqueous solution are added stagewise during the course of electrolysis. The pH is maintained at 5.4 to 5.7 and not exceeding 6 by the addition of sulphuric acid or hydrochloric acid to the catholyte. 20 per cent. sulphuric acid or hydrochloric acid is used as anolyte. Lead is the anode and a copper cylindrical amalgamated rotating cathode is used so as to have a peripheral velocity of 176 to 235 metres per minute. A cathodic current density of 2 to 15 amp/dm², but preferably about 12 amp/dm² is used and electrolysis carried out for the theoretical period of time at a temperature not exceeding 25°C. When the reductions were carried out in this way, a current efficiency of 52 to 55 per cent. was obtained on a small scale and about 50 per cent. on a large scale.

Recovery of products :

Attempts have now been made to account for the unreduced salicylic acid so that a material yield of 65 to 70 per cent. of salicylaldehyde has been obtained. After the electrolysis is over, the electrolyte is neutralised with sulphuric acid or hydrochloric acid and steam-distilled. The salicylaldehyde is obtained as an oily layer. The sulphur dioxide evolved is absorbed in soda ash or sodium hydroxide in order to recover the same and the sodium sulphite obtained reused.

The liquor left after steam-distillation on cooling gives a layer of tar from which by reaction with sodium bicarbonate solution a certain amount of salicylic acid is recovered. From the aqueous portion, salicylic acid is recovered by extraction with ether. The salicylic acid thus recovered accounts for about 25 per cent. of the salicylic acid started with. 50 per cent. of the salicylic acid is accounted for as salicylaldehyde. Some amount of a product insoluble in sodium bicarbonate but soluble in alkali is also obtained, whose identity has not been established.

Recovery of boric acid and sodium sulphate :

After ether extraction is over, the aqueous portion is evaporated until sodium sulphate starts separating out. The salt separated is filtered off in the hot state and washed. On cooling boric acid separates out and can be filtered, washed and obtained in a pure condition. In this way, nearly 80 per cent. could be easily recovered and the remaining solution could be reused for making up the electrolyte again. In this way boric acid and sodium sulphate could be reused obtaining sodium sulphate as a by-product. Alternately, the excess sodium sulphate formed only is separated, so that with the original sodium sulphate in solution, it can be used for further reductions along with the boric acid already present.

Anolyte acid :

20 per cent. sulphuric acid is used as anolyte and a highly porous aluminic variety diaphragm helped in the maintenance of strength of acid constant. The sulphuric acid anolyte can be used over and over.

Diaphragm material :

Aluminic variety highly porous diaphragm or diaphragm made of collodion serves the purpose very well.

Use of sodium Chloride as electrolyte instead of sodium sulphate :

Instead of sodium sulphate, sodium chloride can

chloric acid to the catholyte and the catholyte is neutralized, finally with concentrated hydrochloric acid. The recovery of sulphur dioxide and aldehyde is carried out in substantially the same way as before as also the recovery of boric acid, sodium chloride and unreduced salicylic acid.

EXAMPLE 1.

20 g. sodium sulphate, 15 g. boric acid in 140 cc. water is taken as catholyte. 14 g. sodium sulphite and 13.8 g. salicylic acid in 45 cc. water are added in 7 cc. lots every 5 minutes. An amalgamated copper cylinder (0.5 dm² area) is used as cathode. 60 cc. of 20 per cent. H₂SO₄ is used as anolyte in a porous pot (medium porosity). A current of 6 amp. is passed for theoretical time at a temperature of 12°-16°C. Nearly 10-13 cc. of 12N H₂SO₄ is added to catholyte during electrolysis to maintain the pH at 5.7 to 6.0. The catholyte is neutralised with 6 cc. of concentrated H₂SO₄ and steam-distilled to recover the salicylaldehyde. 5.6 cc. was obtained accounting for 52.8 per cent. current efficiency.

EXAMPLE 2.

Using collodion diaphragm and repeating the above experiment only about 5 to 6 cc. of 12N sulphuric acid had to be added in order to maintain the pH. The yield of salicylaldehyde was 5.6 cc. 52.8 per cent.

Large scale laboratory experiment :

The cell set up had a capacity of half a pound of salicylaldehyde in 3 hours or 4 lbs. per day of 24 hours and is shown in sheet one as Figure 1 and Figure 2 of drawing accompanying the Provisional Specification (sectional and top views respectively). The cell container H is of hard rubber. Two aluminic variety highly porous cylindrical diaphragms D, D are kept on either side of the rotating cylindrical cathode C. The porous pots are resting on perspex tripods T, T. Two lead cooling coils F pass through openings E, in the wooden lid W. Two cylindrical lead anodes A, A are kept inside the porous pots. The cathode is fabricated from 1/16" thick copper plate by making it cylindrical and welding the edge. A wooden core is used and the ends waxed. A 3/8" copper rod is fitted to the top and connection from this to the copper sheet is made so that two brushes B, B make contact on this rod for the cathode. A glass guide G clamped tightly served to give smooth rotation. A 1/16th H.P. motor with a variac served to control the r.p.m. An opening K, in the lid was used for the addition of solutions during the reduction. Cold fingers are also used in the anode chambers to control the temperature (cold finger: a device for circulation of cold water; a narrow tube sealed into a closed wider tube having an outlet near the sealed end. The narrow tube reaches almost the bottom of the wider tube).

EXAMPLE 3.

The cylindrical cathode 3" diameter was rotated at 800 to 1000 r.p.m. 800 g. of sodium sulphate dissolved to give 5200 cc. solution was used. 600 g. boric acid was added. 552 g. salicylic acid and 560 g. of sodium sulphite are dissolved in 1400 cc. water so that nearly 2 litres of solution are obtained. A current of 70-72 amp. are passed and 135 cc. of the above are added once in 10 minutes. The pH. was maintained at 5.7 to 6.0 by the addition during electrolysis of nearly 150 cc. of 12N sulphuric acid. 700 cc. of 20 per cent. H₂SO₄ in each porous pot was the anolyte and this was increased to one litre in each during electrolysis. Temperature was 15°-18°C. Cell voltage was 14 to 15 volts.

Isolation products :

240 cc. concentrated sulphuric acid was used for neutralising the catholyte and steam-distilled to obtain 244 g. salicylaldehyde (current efficiency, 50 per cent.). 136 g. salicylic acid was also recovered (25 per cent.) nearly. The material yield works up nearly to 75 per cent. The energy consumption is 6 k.w.h.r. (D.C.)/lb. of

EXAMPLE 4.

20 g. sodium chloride and 15 g. boric acid are taken in 140 cc. water as catholyte. 75 cc. of 20 per cent. hydrochloric acid is anolyte in a porous pot with graphite anode. The chlorine evolved at the anode is sucked through alkali. Amalgamated brass cathode (0.5 dm² area) is used. 13.8 g. salicylic acid and 15 g. Na₂SO₃ in 35 cc. water, is added in 6 cc. lots during reduction. Concentrated HCl was added to maintain the pH at 5.7. 6 amp. current was passed for theoretical time. Temperature was 12°-16°C. and cell-voltage 8 volts. The catholyte was neutralized by HCl and the SO₂ recovered and the aldehyde steam-distilled, 5.5 gms. (C.E. 45 per cent.). Unreduced salicylic acid was recovered by ether extraction, 4.1 g. The sodium chloride and boric acid are recovered by the same procedure as described for recovery of sodium sulphate and boric acid. Material yield=65 per cent.

We claim :

1. A process for the preparation of salicylaldehyde which consists in the electrolytic reduction of salicylic acid using sodium sulphate or sodium chloride as electrolyte in the presence of boric acid and wherein a critical pH range, 5.4 to 6.0 is maintained, preferably at 5.7 at a temperature not exceeding 25°C. and using a current density range of 2 to 15 amp/dm² and wherein an aqueous solution of salicylic acid and sodium sulphite (resulting in the formation *in situ* of sodium salicylate and sodium bisulphite in aqueous solution) is added to the catholyte.

2. A process as claimed in Claim 1 wherein the aqueous solution of salicylic acid and sodium sulphite is added to the catholyte stage-wise, the quantity added being proportional to the current passed during electrolysis.

3. A process as claimed in Claim 1 or 2 wherein reduction is carried out at a rotating amalgamated cylindrical cathode at a temperature not exceeding 25°C. using a current density range of 2 to 15 amp/dm² keeping a critical catholyte pH range of 5.4 to 6 but preferably 5.7.

4. A process as claimed in any of the preceding claims wherein aldehyde is separated after electrolysis by neutralizing the catholyte with sulphuric acid or hydrochloric acid and steam-distilling.

5. A process as claimed in any of the preceding claims wherein the sulphur dioxide evolved during steam distillation is recovered as sodium sulphite by bubbling the same into soda ash or alkali.

6. A process as claimed in any of the preceding claims wherein unreduced salicylic acid is recovered by solvent extraction of the catholyte which has been steam distilled as in Claim 4.

7. A process as claimed in any of the preceding claims wherein sodium sulphate or sodium chloride is recovered by concentration of the electrolyte after solvent extraction and filtering hot.

8. A process as claimed in any of the preceding claims wherein boric acid is recovered by cooling the hot filtrate.

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Dated this 18th day of April 1958.

NO. 60864.

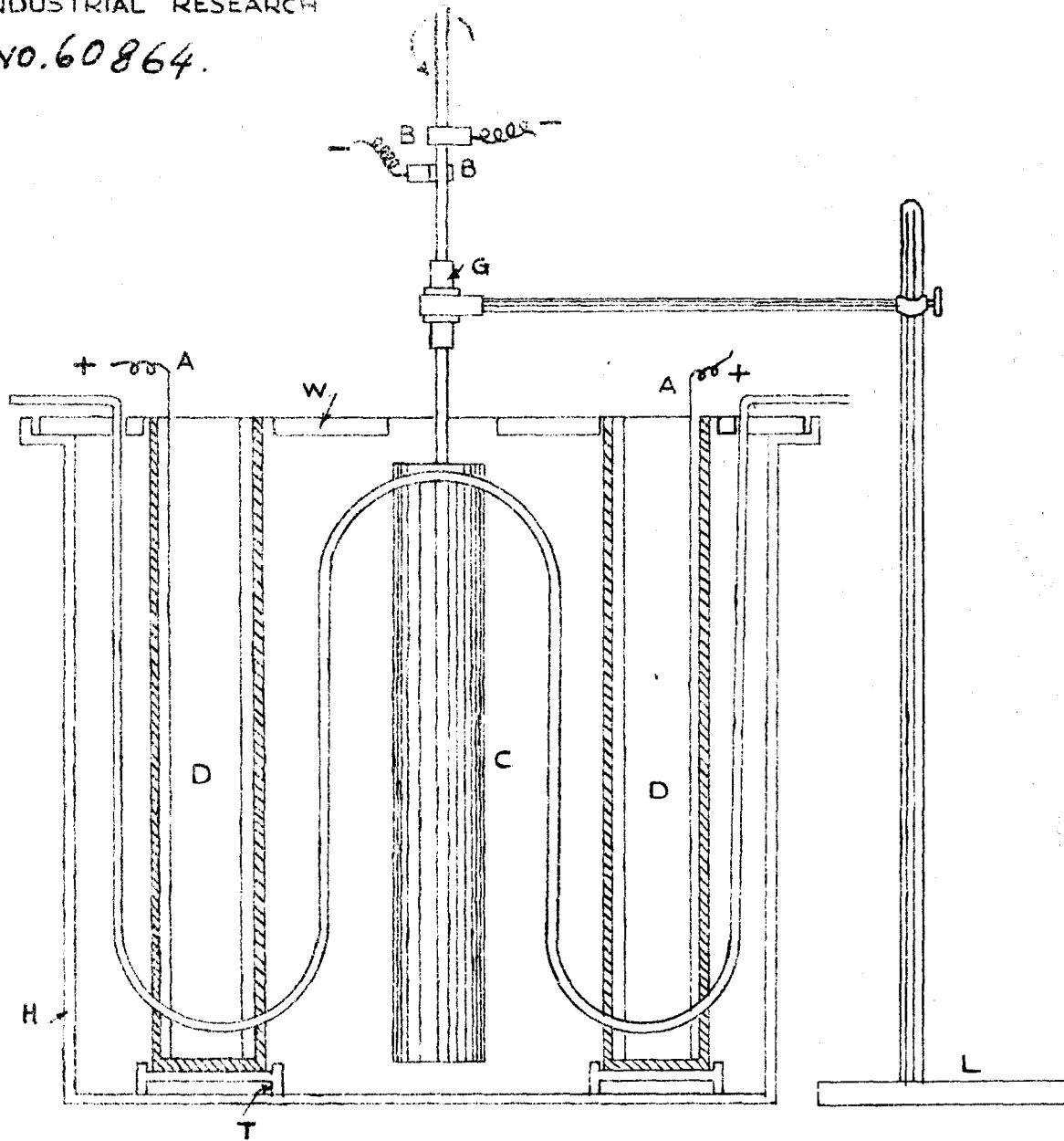


Fig: 1

