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

Specification No. 62379, Application No. 62379, dated 25th November 1957. Complete Specification left on 25th August 1958. (Application accepted 20th May 1959.)

PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN AND OR RELATING TO THE ELECTROLYTIC PREPARATION OF MANGANIC SULPHATE.

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 the invention.

THIS IS AN INVENTION BY HANDADY VENKATAKRISHNA UDUPA, MYSORE SHESHAIYER VENKATACHALAPATHI AND RENGANATHAN RAMASWAMY ALL OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, ALL INDIAN CITIZENS.

The oxidation of manganese sulphate, both chemically and electrolytically in presence of sulphuric acid to obtain different oxidation products of manganese is well known. The use of manganous sulphate as a " carrier " in the electrolytic oxidation of toluene to benzaldehyde has been reported by several earlier workers. The manganous sulphate used in such experiments was in catalytic quantities. The manganic sulphate produced electrolytically from it was reported to bring about the oxidation of toluene and the manganous sulphate formed in the reaction was re-oxidised in the cell. Most of the work reported earlier was confined to studies of electrolytes containing manganese sulphate only in solution. Since it is known that the solubility of manganous sulphate is considerably reduced with increasing strength of sulphuric acid, it was considered useful to investigate systems in which the limitations arising from this could be overcome.

All the earlier workers used stationary anodes in their experiments. An attempt to use the rotating anode was first made by Dey and Maller who reported no improvement in the yield. In the initial stages of the present investigation, a clear solution of manganous sulphate in 53 to 55 per cent. sulphuric acid was used in the electrolytic cell and the manganic sulphate obtained by oxidation was used in a separate vessel for the oxidation of organic compounds such as oxidation of toluene to benzaldehyde. The manganous sulphate formed was reoxidised to manganic sulphate in the electrolytic cell and used again for oxidation of a further quantity of organic compound. In this way, the process is made continuous and cyclic, the manganous sulphate and sulphuric acid being used in a number of experiments. By this operation, however, it was soon observed that the efficiency of oxidation of manganous to manganic sulphate decreased considerably in subsequent operations which was traced to the presence of organic substances in the acid. The first improvement which was effected, therefore, consisted in giving a vacuum treatment to the electrolyte after it was used in the oxidation step so that a few ml. which contained all the volatile organic matter was distilled off. The remaining electrolyte was again made up to strength and oxidised in the electrolytic cell. In this way it was possible to maintain the oxidation efficiency of manganous sulphate at about 80 to 90 per cent.

The amount of manganous sulphate soluble in 53 per cent. sulphuric acid is about 4 per cent. so that a large volume of acid would have to be handled in order to have a sufficient amount of manganic sulphate for practical scale production. A simple calculation would indicate that a volume of nearly 152 litres of acid would be required, for example, to produce 1 lb. of benzaldehyde per charge on the basis of 40 per cent. current efficiency. A second improvement in the process was effected at this stage which consisted in taking a suspension of manganous sulphate in 53 sulphuric acid and oxidising it to manganic sulphate electrolytically and using the paste for the oxidation of organic compounds. In this way, it has now become possible to adopt the process for practical scale production.

The present process, in brief, consists in taking a paste of manganous sulphate (50 to 300 grams per litre) in sulphuric acid (50 to 60 per cent.) and electrolytically oxidising the same to manganic sulphate using lead or antimonial lead anode and cathode in an undivided cell at temperatures of 30° to 100° C. and anodic current density of 1 to 20 amp./dm.^{2}. It is further characterised in that either a stationary anode or a rotating anode is employed in the electrolytic cell. It is further characterised in that after separating the organic product, the suspension of the paste in the acid is given a vacuum treatment whereby the volatile organic matters are removed and the paste returned to the electrolytic cell for re-oxidation, so that the process becomes a cyclic one.

To prepare a free flowing paste of manganous sulphate in 53 per cent. sulphuric acid, a paste of manganous sulphate in water is made first. The required quantity of this aqueous paste is added to 55 per cent. sulphuric acid so as to get a final acid strength of 53 per cent. This is the paste used in the electrolytic cell.

ELECTROLYTIC CELLS.

(a) *Stationary Anode Cell* :

On a small scale a lead sheet bent into a cylindrical form is kept inside a one litre tall form beaker with a small strip of lead cathode towards the open end of the same, anode to cathode area being 18:1. A glass stirrer is used for agitation of the contents. A wooden lid with suitable openings for the stirrer thermometer, anode and cathode leads covers the beakwer.

(b) *Rotating Anode Cell* :

The same strip of metal is used as cathode and a cylindrical lead anode (1" diam) is used for oxidation. A wooden core covered with lead sheet and supported by a ¼" copper rod is the design for the anode. The rotation of the anode itself helps to bring about sufficient agitation of the reaction mixture. As before, a wooden lid with suitable openings for thermometer, cathode and anode leads covers the beaker.

ELECTROLYSIS.

700 cc. of 53 per cent. sulphuric acid containing 200 gms. of manganous sulphate was electrolysed at an anodic current density of 1 to 20 amp./dm.^{2}, *for the theoretical period of time,* at temperatures ranging from 35° to 90° C. The strength of acid used varied between 53 to 65 per cent. and the manganous sulphate content of the electrolyte between 50 to 300 g/1. On increasing the current density from 1 to 20 amp./dm.^{2}, current efficiency dropped from 78·2 per cent. to 60·2 per cent. for stationary anode and from 84·9 per cent. to 63·5 per cent. for rotating anode. Using rotating anode, the temperature of oxidation was varied from 30° to 90° C. but there was no substantial effect at all on the current efficiency of the process. From 53 to 60 per cent. acid, the

current efficiency virtually remained the same, but there was an increase in cell voltage. Using 65 per cent. acid resulted in a considerable increase of cell voltage and also a lowering of current efficiency. The preferred conditions for obtaining best results are 53 per cent. sulphuric acid containing 300 gms. per litre manganous sulphate electrolytically oxidised at 40° to 50° C., using an anodic current density of 10 amp./dm.^{2} at a rotating lead or antimonial lead or antimonial lead anode. 80 to 85 per cent. current efficiency was obtained and excess current was passed to obtain 100% conversion of manganous to manganic sulphate before it was used in the oxidation of organic compounds. Increasing the amount of manganous sulphate beyond 300 gms. per litre leads to too hard a paste and to a considerable increase of cell voltage.

Regeneration of Manganic Sulphate from the Paste used in the Oxidation of Organic Compounds :

The paste after separation of the organic compound followed (if necessary) by extraction with a solvent is charged into a vacuum kettle and subjected to distillation under reduced pressure. The organic volatile compounds are removed along with some water. Residual paste of manganous sulphate in sulphuric acid is once again adjusted to the required acid strength and then re-used for oxidation to manganic sulphate and the whole cycle of operations continued. A comparison of the current efficiency of oxidation of manganous sulphate to manganic sulphate using stationary and rotating anodes is given in the following table :

Cell Voltage (volts)	c.d. (amp/dm^2)	Current efficiency (per cent) Stationary.	Rotating.
2·9	5	78·2	84·9
3·3	10	77·4	83·0
3·6	15	71·4	74·1
4·0	20	60·2	63·8

EXAMPLE

200 grams of manganous sulphate in 700 cc. of 55 per cent. sulphuric acid was oxidised by passing 44 amp.-hrs. at 5 amp./dm.^{2} at 50° to 55° C. using rotating lead anode (1" diam., the anode area immersed being 1·2 dm.^{2}). The inter-electrode distance was 3 cm. and the ratio of anode to cathode area was 18:1. The cell voltage was 2·9 to 3 volts. Current efficiency of oxidation was 84·9 per cent.

R. BHASKAR PAI,

Patent Officer,

Council of Scientific and Industrial Research.

Dated this 22nd day of November 1957.

COMPLETE SPECIFICATION

IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC PREPARATION OF MANGANIC SULPHATE.

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, MYSORE SHESHAIYER VENKATACHALAPATHI AND RENGANATHAN RAMASWAMY ALL OF THE CENTRAL ELECTRO-CHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, ALL INDIAN CITIZENS.

This invention relates to improvements in or relating to the electrolytic preparation of manganic sulphate.

The oxidation of manganese sulphate, both chemically and electrolytically in presence of sulphuric acid to obtain manganic sulphate solutions is well known. The manganous sulphate used in such experiments was in catalytic quantities, *i.e.*, of the order of 2 to 4 per cent., which gave manganese sulphate only in solution. This was open to the drawback that in the solution form, the oxidising agent, namely, manganic sulphate, could be obtained only in a very dilute form (*i.e.*, of the order of only 2 to 4 per cent. as just mentioned), which made it uneconomical for commercial utilization of the manganic sulphate solution for the subsequent oxidation of organic compounds, *e.g.*, oxidation of toluene to benzaldehyde. Thus the amount of manganous sulphate soluble in 53 per cent. sulphuric acid being about 4 per cent., a large volume of acid would have to be handled in order to have a sufficient amount of manganic sulphate for practical scale production. A simple calculation would indicate that a volume of nearly 152 litres of acid would be required, for example, to produce 1 lb. of benzaldehyde per charge on the basis of 40 per cent. current efficiency.

Secondly, while most of the earlier workers used stationary anodes in their experiments, an attempt to use the rotating anode first made by Dey and Maller, resulted in no improvement in the yield.

Thirdly, in the hitherto known process if the manganous sulphate left after the oxidation of an organic compound is used for re-oxidation to manganic sulphate in an electrolytic cell, high efficiency of oxidation could not be maintained, due to the presence of organic substances in the electrolyte. This has been a serious drawback in the way of making the process continuous and cyclic. Thus, we carried out a few initial studies using a clear solution of manganous sulphate in 53 to 55 per cent. sulphuric acid in the electrolytic cell. The manganic sulphate obtained by oxidation was used in a separate vessel for the oxidation of organic compounds such as oxidation of toluene to benzaldehyde. The manganous sulphate formed was reoxidised to manganic sulphate in the electrolytic cell and used again for oxidation of a further quantity of organic compound. In this way, the process is made continuous and cyclic, the manganous sulphate and sulphuric acid being used in a number of experiments. By this operation, however, it was soon observed that the efficiency of oxidation of manganous to manganic sulphate decreased considerably in subsequent operations which was traced to the presence of organic substances in the acid.

We have found that the use of a *suspension* of manganous sulphate instead of a *solution* of manganous sulphate in the electrolytic oxidation of manganous sulphate results in the unforeseen advantage of obtaining a concentrated form of the oxidising agent, namely, manganic sulphate of the order of 6 to 40 per cent. concentration. This has opened up the possibility of utilizing the resulting suspension (or paste) or manganic sulphate for the oxidation of organic compounds, *e.g.*, of toluene to benzaldehyde.

Further, we have found that in order to make the process continuous and cyclic, a vacuum distillation treatment should be given to the electrolyte (sulphuric acid having the suspension of manganous sulphate) after it has been used in the organic oxidation step so that the electrolyte is freed of all the organic matter.

The remaining electrolyte can be again made up to the original strength of sulphuric acid and re-oxidised in the electrolytic cell. In this way it is possible to maintain the oxidation of manganous sulphate at about 80 to 90 per cent.

The process for the preparation of manganic sulphate by the electrolytic oxidation of manganous sulphate in presence of sulphuric acid is characterised according to the present invention in that manganous sulphate is used in the form of a suspension in sulphuric acid resulting in a suspension of manganic sulphate in sulphuric acid.

The present process, in brief, consists in taking a paste of manganous sulphate (50 to 300 grams per litre) in sulphuric acid (50 to 60 per cent.) and electrolytically oxidising the same to manganic sulphate using lead or antimonial lead or lead oxide anode and lead or antimonial lead as cathode in an undivided cell at temperatures of 30° to 100° C. and anodic current density of 1 to 20 amp./dm.^{2}. It is further characterised in that either a stationary anode or a rotating anode is employed in the electrolytic cell. It is further characterised in that after separating the organic product, the suspension of the paste in the acid is given a vacuum distillation treatment whereby the organic matters are removed and the paste returned to the electrolytic cell for re-oxidation, so that the process becomes continuous and cyclic.

To prepare a free flowing paste of manganous sulphate in 53 per cent. sulphuric acid, a paste of manganous sulphate in water is made first. The required quantity of this aqueous paste is added to 55 per cent. sulphuric acid so as to get a final acid strength of 53 per cent. This is the paste used in the electrolytic cell.

ELECTROLYTIC CELLS.

(a) *Stationary Anode Cell* :

On a small scale a lead sheet bent into a cylindrical form is kept inside a one litre tall form beaker with a small strip of lead cathode towards the open end of the same, anode to cathode area being 18:1. A glass stirrer is used for agitation of the contents. A wooden lid with suitable openings for the stirrer thermometer, anode and cathode leads covers the beaker.

(b) *Rotating Anode Cell* :

The same strip of metal is used as cathode and a cylindrical lead anode (1″ diam.) is used for oxidation. A wooden core covered with lead sheet and supported by a 1/4″ copper rod is the design for the anode. The rotation of the anode itself helps to bring about sufficient agitation of the reaction mixture. As before, a wooden lid with suitable openings for thermometer cathode and anode leads covers the beaker.

Electrolysis.

700 cc. of 53 per cent. sulphuric acid containing 200 gms. of manganous sulphate was electrolysed at an anodic current density of 1 to 20 amp./dm.^{2}, *for the theoretical period of time,* at temperatures ranging from 35° to 90° C. The strength of acid used varied between 53 to 65 per cent. and the manganous sulphate content of the electrolyte between 50 to 300 g./1. On increasing the current density from 1 to 20 amp./dm.^{2}, current efficiency dropped from 78·2 per cent. to 60·2 per cent. for stationary anode and from 84·9 per cent. to 63·5 per cent. for rotating anode. Using rotating anode, the temperature of oxidation was varied from 30° to 90° C. but there was no substantial effect at all on the current efficiency of the process. From 53 to 60 per cent. acid, the current efficiency virtually remained the same, but there was an increase in cell voltage. Using 65 per cent. acid resulted in a considerable increase of cell voltage and also a lowering of current efficiency. The preferred conditions for obtaining best results are 53 per cent. sulphuric acid containing 300 gms. per litre manganous sulphate electrolytically oxidised at 40° to 50° C., using an anodic current density of 10 amps./dm.^{2} at a rotating lead or antimonial lead anode. 80 to 85 per cent. current efficiency was obtained and excess current was passed to obtain 100 per cent. conversion of manganous to manganic sulphate before it was used in the oxidation of organic compounds. Increasing the amount of manganous sulphate beyond 300 gms. per litre leads to too hard a paste and to a considerable increase of cell voltage.

Regeneration of Manganic Sulphate from the Paste used in the Oxidation of Organic Compounds :

The paste after separation of the organic compound followed (if necessary) by extraction with a solvent is charged into a vacuum kettle and subjected to distillation under reduced pressure. The organic volatile compounds are removed along with some water. Residual paste of manganous sulphate in sulphuric acid is once again adjusted to the required acid strength and then re-used for oxidation to manganic sulphate and the whole cycle of operations continued. A comparison of the current efficiency of oxidation of manganous sulphate to manganic sulphate using stationary and rotating anodes is given in the following table :

Cell Voltage (volts)	c. d. (amp/dm^2)	Current efficiency (per cent)	
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EXAMPLE

200 grams of manganous sulphate in 700 cc. of 55 per cent. sulphuric acid was oxidised by passing 44 amp./hrs. at 5 am./dm.^{2} at 50° to 55° C. using rotating lead anode (1″ diam., the anode area immersed being 1·2 dm.^{2}). The inter-electrode distance was 3 cm. and the ratio of anode to cathode area was 18:1. The cell voltage was 2·9 to 3 volts. Current efficiency of oxidation was 84·9 per cent.

It has been found that in addition to the use of lead or antimonial lead as anode, electrolytically deposited lead dioxide can also be used. An example of the same is given (example IV).

Large laboratory scale trials :

The apparatus used for the large laboratory scale preparation of manganic sulphate starting with a paste of manganous sulphate in 55 per cent. sulphuric acid is shown in the accompanying drawings. Figure 1 is the arrangement for the *rotating lead anodes.* A cylindrical wooden core lined completely with lead sheet served as anode A. This is attached to the lower end of a rotating shaft B by means of clamps C. The rotating shaft B is supported by a flat angle-iron framework E having suitable ball-bearing F. The rotating shaft has a mercury cup G on top through which the contact is made to the anode by a lead H dipping into the mercury from the anode bus-bar I. Below the mercury cup is pulley J through which a V-belt passes connecting it to the next anode assembly or the motor. The angle-iron framework has flat supports K with slots so that its position may be adjusted suitably and the whole anode is mounted on two parallel horizontal wooden beams L of a stand M. Three or more such anodes can be mounted on the wooden beam depending on the capacity of the cell. The cell-container and the cathodes are not shown in the diagram. A porcelain tank 14″×14″×10·5″ is used as the cell-container in which only two lead anodes are used. The cathodes, 3 for each anode are arranged round the cylindrical anode symmetrically.

A glass sheet immersed in the cell served to separate the two lead anodes along with their respective cathodes. Figure 2 is a plan of the anode assembly used for the rotating anode cell.

The cell set-up for *stationary anode* is shown in Figure 3 which is a sectional front elevation of the same. This consists of a lead-lined wooden container N which itself acts as anode. Four or six number of lead cathodes O are arranged properly and connected together by a bus-bar P so as to give proper current distribution. An ebonite stirrer Q is used for agitating the paste. A quarter H.P. motor R was used for driving the stirrer. A lead cooling coil S may also be used.

EXAMPLE I.

10 litres of 55 per cent. sulphuric acid containing 7 lbs. of manganous sulphate was oxidised at an anodic current density of 10 amp./dm.^{2} and theoretical current was passed using rotating anodes. 80 per cent. current efficiency was obtained at 50° C. The electrolyte after using for oxidation of toluene was given a vacuum treatment and again regenerated under the above experimental conditions to give 75 per cent. current efficiency.

EXAMPLE II.

The experiment was repeated using 20 litre of acid containing 14 lbs. of manganous sulphate. Current efficiency was 79 per cent. and after oxidation of toluene, regeneration gave 78 per cent. current efficiency.

EXAMPLE III.

Using the stationary anode cell 10 litres of 55 per cent. sulphuric acid containing 8 lbs. of manganous sulphate was oxidized at 50° C. using an anode current density of 10 amp./dm.^{2} to give 75 per cent. current efficiency. The electrolyte was then used in the oxidation of toluene to benzaldehyde, recovered and re-oxidized after vacuum treatment to give 74 per cent. and 72 per cent. current efficiency for manganic sulphate formation in subsequent operations.

EXAMPLE IV.

Use of lead-dioxide anode.

700 cc. of 55 per cent. sulphuric acid containing 200 g. of manganous sulphate was oxidized using a cylindrical lead dioxide anode (deposited on graphite rod) at an anodic current density of 10 amp./dm.^{2}. A current efficiency of 79·8 per cent. for manganic sulphate formation was obtained at 50° C.

We claim :

1. A process for the electrolytic preparation of manganic sulphate by the electrolytic oxidation of manganous sulphate in presence of sulphuric acid wherein manganous sulphate is used in the form of a suspension in sulphuric acid resulting in a suspension of manganic sulphate in sulphuric acid.

2. A process as claimed in Claim 1 wherein a suspension of manganous sulphate (from 50 to 350 gm. per litre) in sulphuric acid (50 to 65 per cent. strength) is oxidized in an undivided electrolytic cell.

3. A process as claimed in Claim 1 or 2 wherein the oxidation is brought about at a temperature ranging from 30° to 100° C.

4. A process as claimed in any of the preceding claims wherein a lead or antimonial lead or lead dioxide is uded as anode and lead or antimonial lead is used as cathode.

5. A process as claimed in any of the preceding claims wherein the anode is stationary or rotating and while stationary an auxilliary stirrer is employed.

6. A process as claimed in any of the preceding claims wherein an anodic current density of 1 to 20 amp./dm.^{2} is used.

7. A process as claimed in any of the preceding claims wherein a paste of manganic sulphate is obtained for use in the oxidation of organic compounds.

8. A process as claimed in any of the preceding claims wherein the paste of manganous sulphate in sulphuric acid left after oxidation of organic compounds is re-used for oxidation to manganic sulphate after giving a vacuum distillation treatment whereby volatile organic substances are removed from the same.

9. Manganic sulphate whenever regenerated by electrolytic oxidation of manganous sulphate in sulphuric acid according to a process substantially as hereinbefore described.

R. BHASKAR PAI,

Patents Officer,

Council of Scientific & Industrial Research.

Dated this 22nd day of August 1958.

MGIPC—S3—30 Patent/59—19-4-60—100.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
NO 62379

COMPLETE SPECIFICATION

NO. OF SHEETS.
SHEET NUMBER.

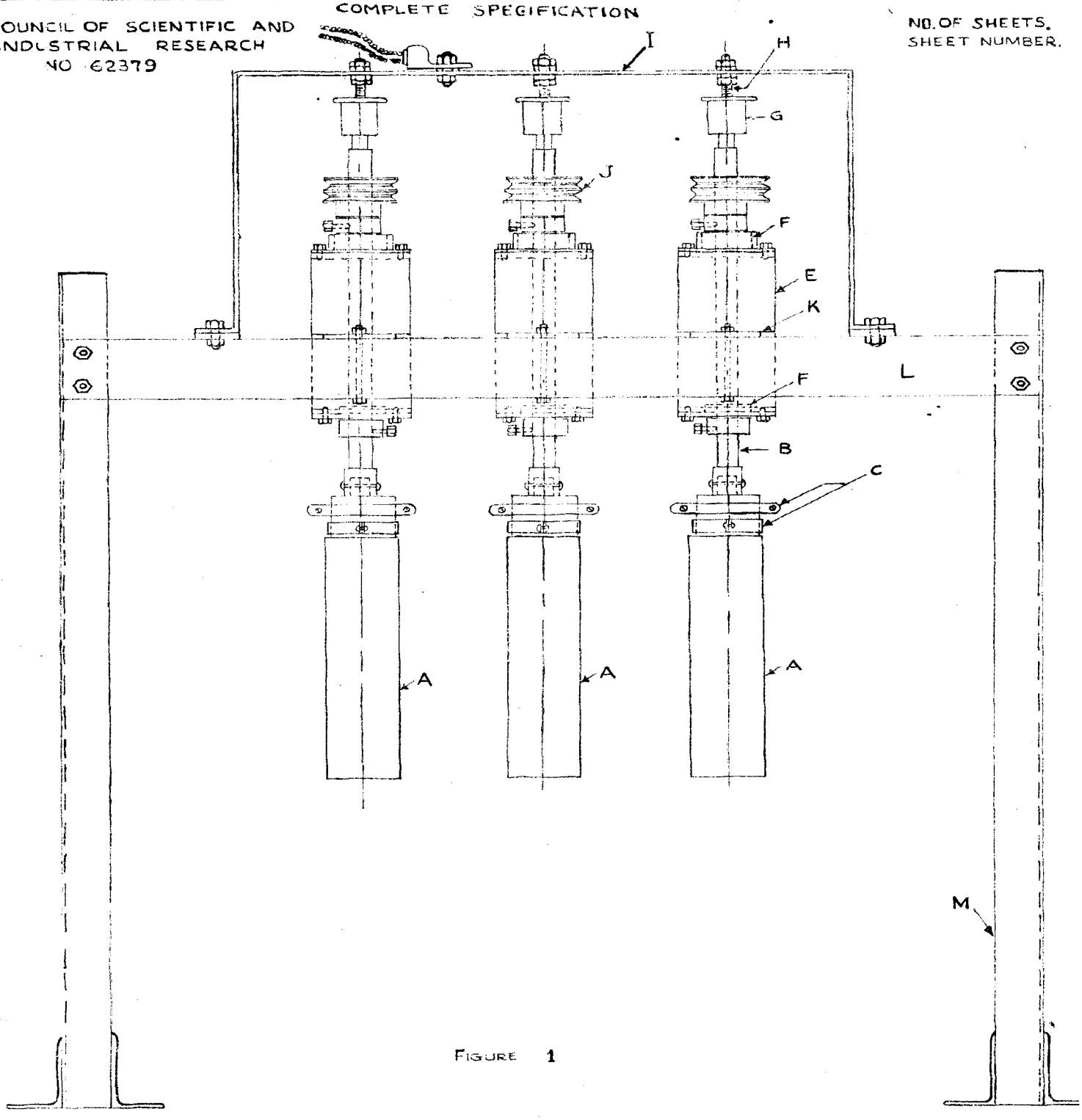

FIGURE 1

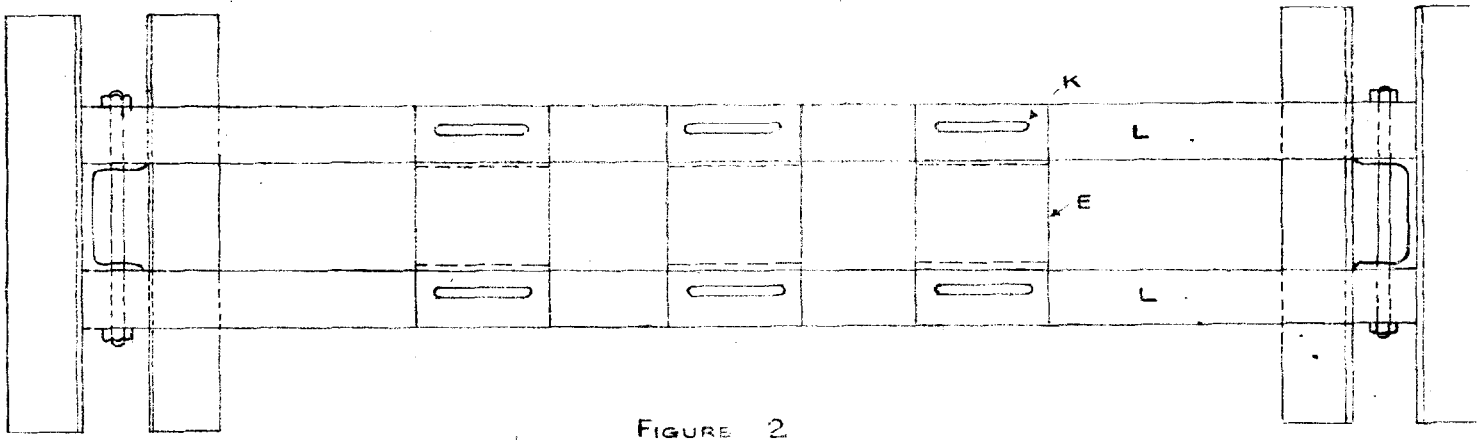

FIGURE 2

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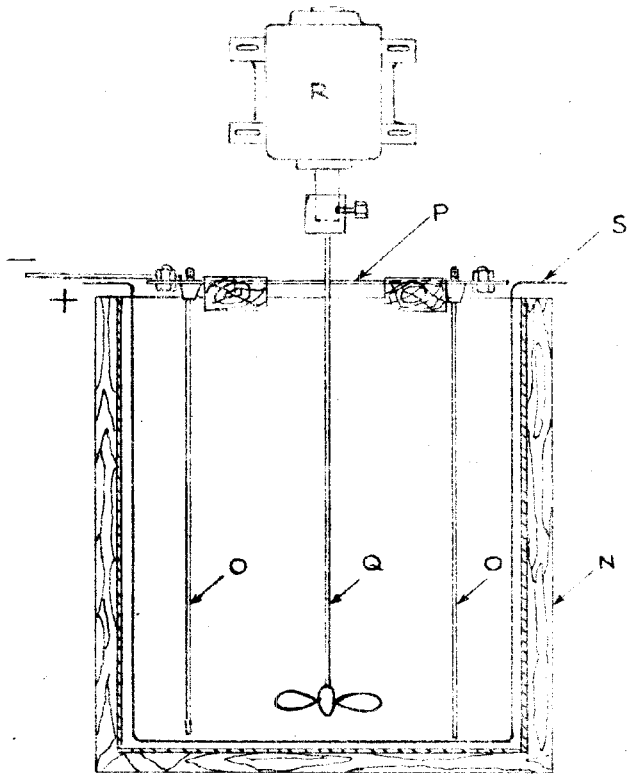

FIGURE 3

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