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PROVISIONAL SPECIFICATION.

A NEW TECHNIQUE FOR THE ELECTROLYTIC PREPARATION OF CUPROUS OXIDE.

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 BIMAN BIHARI DEY, NANDADY VENKATKRISHNA UDUPA, SRINIVASA SAMPATH AND RAMANATHAN VISWANATHAN, all of the Central Electrochemical Research Institute, Karaikudi, India, all Indian citizens.

This invention relates to a process for the electrolytic preparation of cuprous oxide by a new technique.

Cuprous oxide was prepared for the first time by the electrolytic method using stationary anode by Lorenz in 1896, followed later by other workers who mainly tackled the problem from a purely academic view-point. Important process details so essential for manufacture on a practical scale had not been published in detail in the available literature. Some of the details of the process developed in the Central Electrochemical Research Institute, using stationary anodes have already been published. As a result of further investigation carried out in these laboratories a new technique has been developed for the electrolytic preparation of cuprous oxide, the details of which are given in the following paragraphs.

The present invention is characterised in that a new technique of rotating anode is employed for the first time for the electrolytic preparation of cuprous oxide.

Thus, according to the present invention, a solution of sodium chloride and an alkali is electrolysed in a cell with sheet copper as cathode and pure or refined copper as rotating anode.

Preheated (65°C to 95°C, but preferably 80°C) electrolyte, containing not less than 10 per cent. sodium chloride by weight, preferably a saturated sodium chloride solution and 0.3 to 5 gpl. alkali (expressed as sodium hydroxide) are fed into the cathode chambers of an electrolytic cell in which sheet copper is used as cathode and pure or refined copper is employed as rotating anode and wherein the rate of flow of the electrolyte is such that the alkalinity of the bath is always maintained at the specified optimum range, viz., 0.3 gpl. to 5 gpl. expressed as sodium hydroxide.

The main advantage gained by the use of rotating anodes is that a much higher current density than what is the practice at present with the anodes in a stationary condition can be used. The use of high current density in turn leads to a shorter duration of electrolysis which means saving in man-hours and machine-hours during the process of manufacture.

This new technique as has been found can be utilised with advantage even beyond the current density of 5 amp./dm² which happens to be the optimum value for a stationary anode.

The following table gives the comparative data obtained under identical conditions, the current density having been varied from 5 to 20 amp./dm² using both the stationary and rotating anodes for the preparation of cuprous oxide.

Current density (Amp./dm ²)	STATIONARY ANODE.			ROTATING ANODE.		
	Purity.	Energy consumption/lb. Kw. hr.	Colour of Product.	Purity.	Energy consumption/lb. Kw. hr.	Colour of product.
5	Standard (98%)	0.234	Bright red.		0.22	Uniform.
10	Falls below the standard value.	0.27	Lightens in shade.	Standard purity or above.	0.23	Shade throughout the range.
15		0.31			0.29	
20		0.41			0.31	

Saturated sodium chloride solution with 0.6 gpl. alkali (as NaOH) was electrolysed for one hour at 80°C. Rate of circulation was kept constant at the proper value.

As seen from the table the purity of the product obtained is adversely affected by increase in current density at a stationary anode. Product conforming to the Indian Standard Specifications is obtained only when the current density is maintained at 5 amp./dm². But when the anode is rotated, the purity of the product remains high beyond the current density of 5 amp./dm². Also it can be noticed that for a particular current density energy consumption (D.C.) is less at a rotating anode.

A more important point in favour of the rotating anode is that uniformly good results are obtained over a very wide range of current density. The colour of the product is susceptible even to a slight change in current density when the anode is stationary but at a rotating anode the colour of the product remains uniform over a wide range of current density.

By using this new technique it is possible to use a very wide range of current density, say from 5 amps/dm² to 100 amps/dm² and to obtain product of better purity than is obtained at stationary anodes under same current density conditions. Possibility of using high current density also leads to increased cell capacity and thereby leads to lower initial investment and floor space. Alternatively for the same installed cell, a shortening of the duration of the electrolysis could lead to a saving in man-hours and machine-hours and to a cutting down of the cost of heating the electrolyte. Wide range of current density also permits a judicious choice of process conditions depending on the availability and the cost of electricity. More than anything else the new technique also permits a certain adjustability of the plant and the process to produce more for the same installation during off peak hours when power might be supplied cheaper in certain localities.

The invention will now be described with the help of accompanying drawings.

The Electrolytic Cell: (Fig. 1) The cell used in small-scale investigation consists of a glass basin (A) which is kept inside a wooden box (B) and is insulated by filling the space in between with saw-dust. A syphon (C) serves for the removal of the product along with the anolyte. Two diaphragms (D) made of canvas wrapped around a glass-frame (or hard-rubber frame) are supported on either side of the rotating anode (E).

On a large-scale a reinforced cement concrete cell which is a square or circular container (rectangular or oval if more than one anode assembly is to be used) provided with a conical bottom and an opening at the bottom could be used. Glass or glass-lined equipment, asphalt-coated wooden tanks, ceramic-ware or metal containers with suitable protective coating could also be used as cells.

Anode Assembly: The anodes could be (a) a solid rod, e.g., cylindrical rods Fig. 2, (i) (b) pipes Fig. 2, (ii) or sheets bent into a cylindrical form Fig. 2, (iii), (c) strips of sheet copper suspended from suitable balanced arms or from a circular frame; e.g., strips of pure copper sheet suspended from arms as shown in Fig. 2, (iv), Fig. 2(v) and Fig. 2(v.) or (d) copper discs mounted on a copper shaft which is protected from the electrolyte, rotating either vertically Fig. 2(vii) or horizontally Fig. 2(viii).

When only two strips are to be used as anode the set-up as in Fig. 2 (iv) is used. When 4 strips are to be used, the set-up as shown in Fig. 2 (v) is used.

When however, more than 4 strips are to be used the number of arms could be increased in twos so as to get a balanced system for rotation. A ring made out of a flat-strip of copper supported in the centre as in Fig. 2 (v) carrying two, four, six or more strips as per need could also serve as an anode assembly for strips. The width of the strips is to be limited to a value, which as far as possible would form part of the circumference of the circle which the anode forms in its rotation inside the anolyte. If the strip is too wide then the movement of the strip through the anolyte would lead to too much of turbulence and the anode surface would not have the desired metal-liquid shear. The strips may however be so bent as to make the surface of the strips conform to portions of the circumference of the circle which the anode forms within the anolyte during its rotation. The number of strips could be increased with the idea of increasing the anode area as well as the cell-capacity, with this limit that the sum total of the width of the strips could be equal to the circumference of a cylindrical anode of the same diameter as the ring on which they are mounted.

In the case of the rod anode, the diameter of the rod continuously decreases during the course of electrolysis with consequent rise in the current density of the anode. Use of disc-type anodes needs also similar and other situations to be considered. Cylindrical anodes of pipes or sheets bent into cylindrical forms are ideal for the purpose. The only change of dimension that occurs in these and in strip anodes is in the thickness of the strips or the sheet and the slight variation in current density due to this will not be of much consequence.

The anode assembly is supported by means of a vertical rod (F) which is supported by bearings, (G, G) (tapered bearings, if necessary, to support the weight of the anode assembly) fitted on a u-shaped frame (U) and which can be rotated by means of pulleys (H, H) and motor (I) arrangement as shown in Fig. 1. Contact for the anode terminal is made through a mercury cup (J) fitted on top of the rod (F). On a large-scale carbon brush contact on the rod (F) would also serve the purpose.

Auxiliary Equipments: *Heating Tank:* Electrolyte is fed into this 2-litre beaker (K) supported on a tripod stand (L) which is heated by means of a bunsen burner (M) in order to raise the temperature to the required level. On a large-scale suitable size tanks heated either by steam or electricity are employed.

Syphon: A syphon (N) serves to feed the electrolyte into the cathode chambers via the feeding arrangement (O). On a large-scale a pump may be used to feed the electrolyte into a constant-head tank from where it may be circulated into the cathode chambers.

Filtering Apparatus: Sintered-glass funnels (G 3 porosity) are used on a small-scale, for filtering the product by applying suction. On a large-scale rotary suction filters or filter presses and centrifuges are to be employed.

Operation: The hot electrolyte is fed into the two cathode compartments at a steady predetermined rate. The rate of feeding of electrolyte is a function of the ratio of anolyte to catholyte and the current strength. Electrolyte containing cuprous oxide in suspension is withdrawn by syphon (N) in order to maintain constant level and the product filtered off. The clear liquor is fed into the heating tank (K) from where it is fed back into the cell after heating to the required temperature. The product in the filter is washed free of adhering electrolyte and dried at 100°C preferably under reduced pressure.

Conditions of Electrolysis: The electrolyte contains 10 to 25 per cent. by weight of sodium chloride and 0.3 to 5 gpl of alkali expressed as sodium hydroxide. Increasing the sodium chloride concentration helps in reducing the cell-voltages and consequently the energy consumption of the process, using both stationary as well as rotating anode. Thus, using a rotating rod anode of 1/2" diameter, at a current density of 20 amps/dm² the cell-voltages in 10, 18 and 22 per cent. sodium chloride solution were 2 to 2.8, 2 to 2.4 and 1.8 to 2.2 volts respectively. Using the rotating strip anode as per Fig. 2 (iv) (width of strips 0.5 in.) at the same cur-

rent density, the cell-voltage in 10, 18, 22 and 25 per cent. sodium chloride solutions were 2.25 to 2.5, 2.25 to 2.5 and 1.75 volts respectively. Electrolysis was carried out at temperatures of 65°C, to 95°C, but preferably at 80°C.

Electrode Materials: Sheet copper is used as cathode. Either pure or refined copper is employed as anode.

Current Density: An anodic current density of over 5 amps/dm² to 100 amps/dm² or beyond is used with a view to shorten the duration of the process as well as to increase the cell capacity and permitting a judicious choice of process conditions depending on the availability and the cost of electricity. Thus, using a rotating anode, current densities of 5 amps/dm² to 100 amps/dm² could be employed without the efficiency of the process or the purity of the product suffering in any way. The use of such high current densities would also help in increasing the cell capacity considerably, thereby reducing the initial investment on the cells. The cell-voltage and energy consumption using a tubular anode as per Fig. 2 (iii) (diameter 1/2" made out of 1/16" copper sheet) at increasing current densities are given below in a 25 per cent. sodium chloride solution:

C. D. amp/dm ²	Cell-voltage volts	Energy consumption kw. hr/10. (D.C.)
20	1.75	0.30
50	2.75	0.47
100	3.25	0.55

Such high current densities cannot be used when the anode is stationary, because the efficiency of the process as well as the purity of the product suffer.

R.P.M. of anode: When the rod-type anode is employed, both the current density as well the peripheral speed of the anode increase due to corrosion and hence experimental conditions cannot be rigidly controlled. Similar situations arise in the case of disc-type anodes where the current distribution would be odd. When tubular or strip anodes are used the peripheral speed of the anode surface will remain fairly constant. The r.p.m. of the anode will therefore depend upon the diameter of the anode. It has been observed that a peripheral velocity (anode surface velocity) of 10 to 60 metres/min. through the electrolyte, gives a good grade of cuprous oxide. Beyond this range the results obtained are not very satisfactory.

Ratio of anolyte to catholyte: This naturally would vary with the design of the cell and is one of the factors controlling the rate of circulation of the electrolyte. In the small-scale laboratory investigation volume of catholyte was 50 cc and that of anolyte was 450 cc.

Rate of circulation: There is a build-up of alkali at the cathode during electrolysis and this has to be dissipated into the main body of the anolyte which gets depleted in alkali. The quantity of current passed also determines the alkali build-up so that the rate of flow of electrolyte is so adjusted as to maintain the desired alkalinity in the anolyte.

Diaphragm material: Cloth diaphragm was found to be most suitable for the purpose. It effectively prevents cuprous oxide from moving to the cathode and getting reduced as spongy copper but at the same time allows the electrolyte to flow through freely. It does not also offer too great a resistance for passage of current. The diaphragm is supported by means of a frame made of glass, wood or hard-rubber or some suitable material.

Circulation and feed arrangements: From the heating tank (or a constant head tank, on a large-scale) the brine flows into the cell at a specified rate, by careful control. The electrolyte is fed into the cathode compartments by means of tubes branching from a common header tube connected to the tank.

EXAMPLES.

Example I: 25% sodium chloride solution with 0.6 gpl. alkali was used. Anode of diameter 1.25 cms. was rotated at 1000 r.p.m. with a peripheral speed of 39 metre/min. Rate of circulation was 5.0 litres/hr. at a current of 6.0 amps. Current density was 20 amps/dm². Temperature was 80°C and the cell voltage 1.75 volts. Current efficiency for a duration of one hour was

was quantitative and 16.5 gms of cuprous oxide was obtained as red powder. Energy consumption was 0.30 kw. hr/lb.

Example II: At 50 amps/dm² the cell voltage was 2.75 volts under the above conditions and the product was orange in colour and 12.36 gms of product was obtained in 3/4 hr. and the energy consumption was 0.47 kw. hr/lb.

Example III: Under the same conditions as above and at 100 amps/dm² the cell-voltage was 3.25 volts and the current efficiency was quantitative and the product was orange in colour. 8.18 gms of cuprous oxide

was obtained in half an hour and the energy consumption was 0.55 kw. hr/lb of the product.

In all the above examples, the same current was passed and the current density was varied by immersing corresponding portion of the anode in the electrolyte. The rate of circulation of electrolyte was kept constant at 5 litres/hr in the last two experiments also.

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COUNCIL OF SCIENTIFIC AND INDUSTRIAL
RESEARCH.

Dated this 10th day of February, 1956.

COMPLETE SPECIFICATION.

A NEW TECHNIQUE FOR THE ELECTROLYTIC PREPARATION OF CUPROUS OXIDE.

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 BIMAN BIHARI DEY, HANDADY VENKATAKRISHNA UDUPA, SRINIVASA SAMPATH AND RAMANATHAN VISWANATHAN, all of the Central Electrochemical Research Institute, Karaikudi, India, all Indian citizens.

This invention relates to a process for the electrolytic preparation of cuprous oxide by a new technique.

Cuprous oxide was prepared for the first time by the electrolytic method using stationary anode by Lorenz in 1896, followed later by other workers who mainly tackled the problem from a purely academic view-point. Important process details so essential for manufacture on a practical scale had not been published in detail in the available literature. Some of the details of the process developed in the Central Electrochemical Research Institute, using stationary anodes have already been published. As a result of further investigation carried out in these laboratories a new technique has been developed for the electrolytic preparation of cuprous oxide, the details of which are given in the following paragraphs.

The present invention is characterised in that a new technique of rotating anode is employed for the first time for the electrolytic preparation of cuprous oxide.

Thus, according to the present invention, a solution of sodium chloride and an alkali is electrolysed in a cell with sheet copper as cathode and pure or refined copper as rotating anode and wherein the state of motion of the anode is specified, viz., that it is rotating.

Preheated (65°C to 95°C, but preferably 80°C) electrolyte containing not less than 10 per cent. sodium chloride by weight, preferably a saturated sodium chloride solution, and 0.3 to 5 gpl alkali (expressed as sodium hydroxide) are fed into the cathode chambers of an electrolytic cell in which sheet copper is used as cathode and pure or refined copper is employed as rotating anode and wherein the rate of flow of the electrolyte is such that the alkalinity of the bath is always maintained at the specified optimum range, viz., 0.3 gpl to 5 gpl expressed as sodium hydroxide.

The main advantage gained by the use of rotating anodes is that a much higher current density than what is the practice at present with the anodes in a stationary condition can be used. The use of high current density in turn leads to a shorter duration of electrolysis which means saving in man-hours and machine-hours during the process of manufacture.

This new technique as has been found can be utilised with advantage even beyond the current density of 5 amp./dm.² which happens to be the optimum value for a stationary anode.

The following table gives the comparative data obtained under identical conditions, the current density having been varied from 5 to 20 amp./dm.² using both

the stationary and rotating anodes for the preparation of cuprous oxide.

Current density (Amp./dm. ²)	STATIONARY ANODE.			ROTATING ANODE.		
	Purity.	Energy consumption/lb. kw. hr.	Colour of product.	Purity.	Energy consumption/lb. Kw. hr.	Colour of product.
5	Standard (96%)	0.234	Bright red.		0.22	Uniform.
10	Falls below the standard value.	0.27	Lightens in shade.	Standard purity or above.	0.23	Shade throughout the range.
15		0.31			0.29	
20		0.41			0.31	

Saturated sodium chloride solution with 0.6 gpl. alkali (as NaOH) was electrolysed for one hour at 80°C. Rate of circulation was kept constant at the proper value.

As seen from the table the purity of the product obtained is adversely affected by increase in current density at a stationary anode. Product conforming to the Indian Standard Specifications is obtained only when the current density is maintained at 5 amp./dm.² But when the anode is rotated, the purity of the product remains high beyond the current density of 5 amp./dm.² Also it can be noticed that for a particular current density energy consumption (D.C.) is less at a rotating anode.

A more important point in favour of the rotating anode is that uniformly good results are obtained over a very wide range of current density. The colour of the product is susceptible even to a slight change in current density when the anode is stationary but at a rotating anode the colour of the product remains uniform over a wide range of current density.

By using this new technique it is possible to use a very wide range of current density, say from 5 amps/dm.² to 100 amps/dm.² and to obtain product of better purity than is obtained at stationary anodes under same current density conditions. Possibility of using high current density also leads to increased cell capacity and thereby leads to lower initial investment and floor space. Alternatively for the same installed cell, a shortening of the duration of the electrolysis could lead to a saving in man-hours and machine-hours and to a cutting down of the cost of heating the electrolyte. Wide range of current density also permits a judicious choice of process conditions depending on the availability and the cost of electricity. More than anything else the new technique also permits a certain adjustability of the plant and the process to produce more for the same installation, during off peak hours when power might be supplied cheaper in certain localities.

The Electrolytic Cell: The invention will now be described with the help of drawings accompanying the provisional specification and also Figs. I and II of accompanying drawings wherein Fig. I shows a longitudinal section and plan of a large-scale cell and Fig. 2 is a flow-sheet of the process. Fig. I of the drawings accompanying the provisional specification shows the cell used in small-scale investigation and consists of a glass basin (A) which is kept inside a wooden box (B) and is insulated by filling the space in between with saw-dust. A syphon (C) serves for the removal of the product along with the anolyte. Two diaphragms (D) made of canvas wrapped around a glass-frame (or hard-rubber frame) are supported on either side of the rotating anode (E).

On a large-scale a reinforced cement concrete cell which is a square or circular container (rectangular or oval if more than one anode assembly is to be used) provided with a conical bottom and an opening at the bottom could be used. Glass or glass-lined equipment, asphalt-coated wooden tanks, ceramic-ware or metal containers with suitable protective coating could also be used as cells.

Anode Assembly: The anodes could be (a) a solid rod, e.g., cylindrical rods Fig. 2, (i) (b) pipes Fig. 2, (i) or sheets bent into a cylindrical form Fig. 2, (iii), (c) strips of sheet copper suspended from suitable balanced arms or from a circular frame; e.g., strips of pure copper sheet suspended from arms as shown in Fig. 2, (iv), Fig. 2 (v) and Fig. 2 (vi) or (d) copper discs mounted on a copper shaft which is protected from the electrolyte, rotating either vertically Fig. 2 (vii) or horizontally Fig. 2 (viii).

When only two strips are to be used as anode the set-up as in Fig. 2 (iv) is used. When 4 strips are to be used, the set-up as shown in Fig. 2 (v) is used. When however, more than 4 strips are to be used, the number of arms could be increased in twos so as to get a balanced system for rotation. A ring made out of a flat-strip of copper supported in the centre as in Fig. 2 (vi) carrying two, four, six or more strips as per need could also serve as an anode assembly for strips. The width of the strips is to be limited to a value, which as far as possible would form part of the circumference of the circle which the anode forms in its rotation inside the anolyte. If the strip is too wide then the movement of the strip through the anolyte would lead to too much of turbulence and the anode surface would not have the desired metal-liquid shear. The strips may however be so bent as to make the surface of the strips conform to portions of the circumference of the circle which the anode forms within the anolyte during its rotation. The number of strips could be increased with the idea of increasing the anode area as well as the cell-capacity, with this limit that the sum total of the width of the strips could be equal to the circumference of a cylindrical anode of the same diameter as the ring on which they are mounted.

In the case of the rod anode, the diameter of the rod continuously decreases during the course of electrolysis with consequent rise in the current density of the anode. Use of disc-type anodes needs also similar and other situations to be considered. Cylindrical anodes of pipes or sheets bent into cylindrical forms are ideal for the purpose. The only change of dimension that occurs in these and in strip anodes is in the thickness of the strips or the sheet and the slight variation in current density due to this will not be of much consequence.

The anode assembly is supported by means of a vertical rod (F) which is supported by bearings (G, G) (tapered bearings, if necessary, to support the weight of the anode assembly) fitted on a u-shaped frame (U) and which can be rotated by means of pulleys (H, H) and motor (I) arrangement as shown in Fig. I. Contact for the anode terminal is made through a mercury cup (J) fitted on top of the rod (F). On a large-scale carbon brush contact on the rod (F) would also serve the purpose.

Auxiliary Equipments: Heating Tank: Electrolyte is fed into this 2-litre beaker (K) supported on a tripod stand (L) which is heated by means of a bunsen burner

(M) in order to raise the temperature to the required level. On a large-scale suitable size tanks heated either by steam or electricity are employed.

Syphon: A syphon (N) serves to feed the electrolyte into the cathode chambers via the feeding arrangement (O). On a large-scale a pumps may be used to feed the electrolyte into a constant-head tank from where it may be circulated into the cathode chambers.

Filtering Apparatus: Sintered-glass funnels (G 3 porosity) are used on a small-scale, for filtering the product by applying suction. On a large-scale rotary suction filters or filter presses and centrifuges are to be employed.

Operation: The hot electrolyte fed into the two cathode compartments at a steady predetermined rate. The rate of feeding of electrolyte is a function of the ratio of anolyte to catholyte and the current strength. Electrolyte containing cuprous oxide in suspension is withdrawn by syphon (N) in order to maintain constant level and the product filtered off. The clear liquor is fed into the heating tank (K) from where it is fed back into the cell after heating to the required temperature. The product in the filter is washed free of adhering electrolyte and dried at 100°C preferably under reduced pressure.

Conditions of Electrolysis: The electrolyte contains 10 to 25 per cent. by weight of sodium chloride and 0.3 to 5 gpl of alkali expressed as sodium hydroxide. Increasing the sodium chloride concentration helps in reducing the cell-voltages and consequently the energy consumption of the process, using both stationary as well as rotating anode. Thus, using a rotating rod anode of 1/2" diameter, at a current density of 20 amps/dm² the cell-voltages in 10, 18 and 22 per cent sodium chloride solution were 2 to 2.3, 2 to 2.4 and 1.8 to 2.2 volts respectively. Using the rotating strip anode as per Fig. 2 (iv) (width of strips 0.5 in.) at the same current density, the cell-voltage in 10, 18, 22 and 25 per cent. sodium chloride solutions were 2.25 to 2.5, 2.25, 2.25 and 1.75 volts respectively. Electrolysis was carried out at temperatures of 65°C to 95°C, but preferably at 80°C.

Electrode Materials: Sheet copper is used as cathode. Either pure or refined copper is employed as anode.

Current Density: An anodic current density of over 5 amps/dm² to 100 amps/dm² or beyond is used with a view to shorten the duration of the process as well as to increase the cell capacity and permitting a judicious choice of process conditions depending on the availability and the cost of electricity. Thus, using a rotating anode, current densities of 5 amps/dm² to 100 amps/dm² could be employed without the efficiency of the process or the purity of the product suffering in any way. The use of such high current densities would also help in increasing the cell capacity considerably, thereby reducing the initial investment on the cells. The cell-voltage and energy consumption using a tubular anode as per Fig. 2 (ii) (diameter 1/2" made out of 1/16" copper sheet) at increasing current densities are given below in a 25 per cent. sodium chloride solution:

C. D. amp/dm ²	Cell-voltage volts	Energy consumption kw. hr/lb. (D. C.)
20	1.75	0.30
50	2.75	0.47
100	3.25	0.55

Such high current densities cannot be used when the anode is stationary, because the efficiency of the process as well as the purity of the product suffer.

R.P.M. of anode: When the rod-type anode is employed, both the current density as well as the peripheral speed of the anode increase due to corrosion and hence experimental conditions cannot be rigidly controlled. Similar situations arise in the case of disc-type anodes where the current distribution would be odd. When tubular or strip anodes are used the peripheral speed of the anode surface will remain fairly constant. The r.p.m. of the anode will therefore depend upon the diameter of the anode. It has been observed that a peripheral velocity (anode surface velocity) of 10 to 60 metres/min. through the electrolyte, gives a good grade of cuprous oxide. Beyond this range the results obtained are not very satisfactory.

Ratio of anolyte to catholyte : This naturally would vary with the design of the cell and is one of the factors controlling the rate of circulation of the electrolyte. In the small-scale laboratory investigation volume of catholyte was 50 cc and that of anolyte was 450 cc.

Rate of circulation: There is a build-up of alkali at the cathode during electrolysis and this has to be dissipated into the main body of the anolyte which gets depleted in alkali. The quantity of current passed also determines the alkali build-up so that the rate of flow of electrolyte is so adjusted as to maintain the desired alkalinity in the anolyte.

Diaphragm material: Cloth diaphragm was found to be most suitable for the purpose. It effectively prevents cuprous oxide from moving to the cathode and getting reduced as spongy copper but at the same time allows the electrolyte to flow through freely. It does not also offer too great a resistance for passage of current. The diaphragm is supported by means of a frame made of glass, wood or hard-rubber or some suitable material.

Circulation and feed arrangements : From the heating tank (or a constant head tank, on a large-scale) the brine flows into the cell at a specified rate, by careful control. The electrolyte is fed into the cathode compartments by means of tubes branching from a common header tube connected to the tank.

EXAMPLES.

Example I : 25% sodium chloride solution with 0.6 gpl alkali was used. Anode of diameter 1.25 cms was rotated at 1000 r.p.m. with a peripheral speed of 39 metre-min. Rate of circulation as 5.0 litres/hr. at a current of 6.0 amps. Current density was 20 amps/dm². Temperature was 80°C and the cell voltage 1.75 volts. Current efficiency for a duration of one hour run was quantitative and 16.5 gms of cuprous oxide was obtained as red powder. Energy consumption was 0.30 kw. hr/lb.

Example II : At 50 amps/dm² the cell voltage was 2.75 volts under the above conditions and the product was orange in colour and 12.36 gms of product was obtained in 3/4 hr. and the energy consumption was 0.47 kw. hr/lb.

Example III : Under the same conditions as above and at 100 amps/dm² the cell-voltage was 3.25 volts and the current efficiency was quantitative and the product was orange in colour. 8.18 gms of cuprous oxide was obtained in half an hour and the energy consumption was 0.55 kw. hr/lb of the product.

In all the above examples, the same current was passed and the current density was varied by immersing corresponding portion of the anode in the electrolyte. The rate of circulation of electrolyte was kept constant at 5 litres/hr in the last two experiments also.

LARGE-SCALE CELL.

Detailed description of the large-scale cell will now be given hereinbelow with reference to accompanying drawings.

Description of the Large-scale cell : (Fig. 1—longitudinal section and plan of the cell): The cell consists of an oval glazed porcelain vessel (A) having a flange and a conical bottom. An opening (C) at the bottom serves for the removal of the product as it is formed. A lid (B) made of perspex covers the cell and carries suitable openings (N, P and I) for the introduction of the supporting framework (O) of the diaphragm (D), the anode (E) and the thermometer. Sheet copper bent suitably is used as cathode (Q) and refined or pure copper sheet is used as anode (E). The bent copper cathode sheets (Q) are suspended inside the diaphragms from an arrangement of busbars (R) as shown in the figure. The bent anode plates (E) are fitted on to a circular frame (S) supported by means of a vertical rod (F) which is fitted with tapered roller-bearings (G) on a frame (U). The anode is rotated by means of a pulley (H) and motor arrangement. Contact for the anode is made through graphitized copper brushes (J) fitted on the top portion of the rod (F). (Z) represents an electrolyte level indicator.

Instead of two diaphragms on either side, 4 diaphragms on four sides of the anode could also be used. The cathode area could thus be increased and a proper

ratio of anodic to cathodic current density could be maintained so as to get economic cell voltages. Contact to the anode could also be made through a mercury cup attached to the top of the rotating shaft. More than one anode assembly could be used in the same cell when cells of larger capacity are required, in which case either a square or rectangular cell with sloping bottom is to be used.

The operation of the Cell : (Fig. 2): Electrolyte (alkaline sodium chloride solution) heated to required temperature in the heating tank (K) is transferred by means of a pump (L) into the constant head tank (M) from where it is fed at optimum rate into the cathode chambers via the feeding arrangement (T, inset in Fig. 2). Electrolyte containing cuprous oxide in suspension is withdrawn by the opening (C) at the bottom of the cell. The product is filtered and filtrate fed back into the cell after heating to required temperature. The product in the filter (V) is washed free of adhering electrolyte and dried (drier, W) at about 100°C preferably under reduced pressure. The dry solid is pulverised and screened (X) before packing (Y).

Example I :

Saturated sodium chloride solution containing 0.6 gpl alkali was circulated at 15 litres/hr. at a temperature of 80°C. A current of 50 amps. was passed for 2½ hours.

Anodic current density	20 amps./dm ²
Anodic C.D. to cathodic C.D. ratio	10:7
Cell-voltage	1.8 volts.
Power consumption (D.C.)/lb of cuprous oxide	0.31 kw-hr.
Product obtained	330 gm.

Purity of product corresponds to I.S. Specification. Colour of the product was bright red.

Example II :

Saturated sodium chloride solution containing 0.6 gpl alkali was circulated at 15 litres/hr. at a temperature of 80°C. A current of 50 amps. was passed for one hour.

Anodic C.D.	50 amps./dm ²
Anodic C.D. to cathodic C.D. ratio	25:7
Cell-voltage	2.7
Power consumption D.C. /lb of cuprous oxide	0.47 kw-hr.
Product obtained	130 gm.

Purity of the product corresponds to I.S. Specification. Colour of the product was brick red.

We claim :

1. A process for the electrolytic preparation of cuprous oxide which consists in electrolysis a solution of sodium chloride and an alkali in a cell with sheet copper as cathode and refined or pure copper as anode and wherein the state of motion of the anode is specified, viz., that it is rotating.
2. A process as claimed in Claim 1 wherein pre-heated electrolyte containing not less than 10% sodium chloride by weight (preferably a saturated solution) and 0.3 to 5 gram per litre alkali (expressed as sodium hydroxide) is fed into the cathode chambers of an electrolytic cell in which sheet copper is used as cathode and pure or refined copper as rotating anode and wherein the rate of flow of the electrolyte is such that the alkalinity of the bath is always maintained at the specified optimum range viz., 0.3 to 5 gpl expressed as sodium hydroxide.
3. A process as claimed in Claim 2 wherein the electrolysis is carried out at temperature of 65°C to 95°C.
4. A process as claimed in Claim 2 wherein the electrolysis is carried out at 80°C.
5. A process as claimed in any of the preceding claims wherein the r.p.m. of the anode is so adjusted as to give an anode surface velocity of 10 to 60 metres/min. through the electrolyte.
6. A process as claimed in any of the preceding claims wherein the rotating anode consists of (a) a

solid rod, (b) a pipe or a sheet bent into a cylindrical form, (c) strips of sheet copper suspended from suitably balanced arms or from a circular frame of (d) discs of copper metal mounted on a copper rod protected from the electrolyte rotating either vertically or horizontally.

7. A process as claimed in any of the preceding claims wherein an anodic current density of over 5 amps/dm² to 100 amps/dm² or beyond is used.

8. A process as claimed in any of the preceding claims wherein constant feeding of electrolyte into the cathode chambers is achieved by means of tubes branching from a common header tube connected to a constant head tank, the level of liquid in which maintains the desired rate of flow into the cell.

9. A process as claimed in any of the preceding claims wherein the electrolysis is carried out in an

electrolytic cell with a conical bottom permitting the removal of the product continuously as it is formed.

10. A process as claimed in any of the preceding claims wherein the rate of feeding of electrolyte is a function of the ratio of anolyte to catholyte and the current strength.

11. A process as claimed in any of the preceding claims wherein the electrolyte (anolyte) along with the product is continuously tapped at the same rate as it is fed, to maintain the required alkalinity in the anolyte.

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Patents Officer,

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Dated this 16th day of October, 1956.

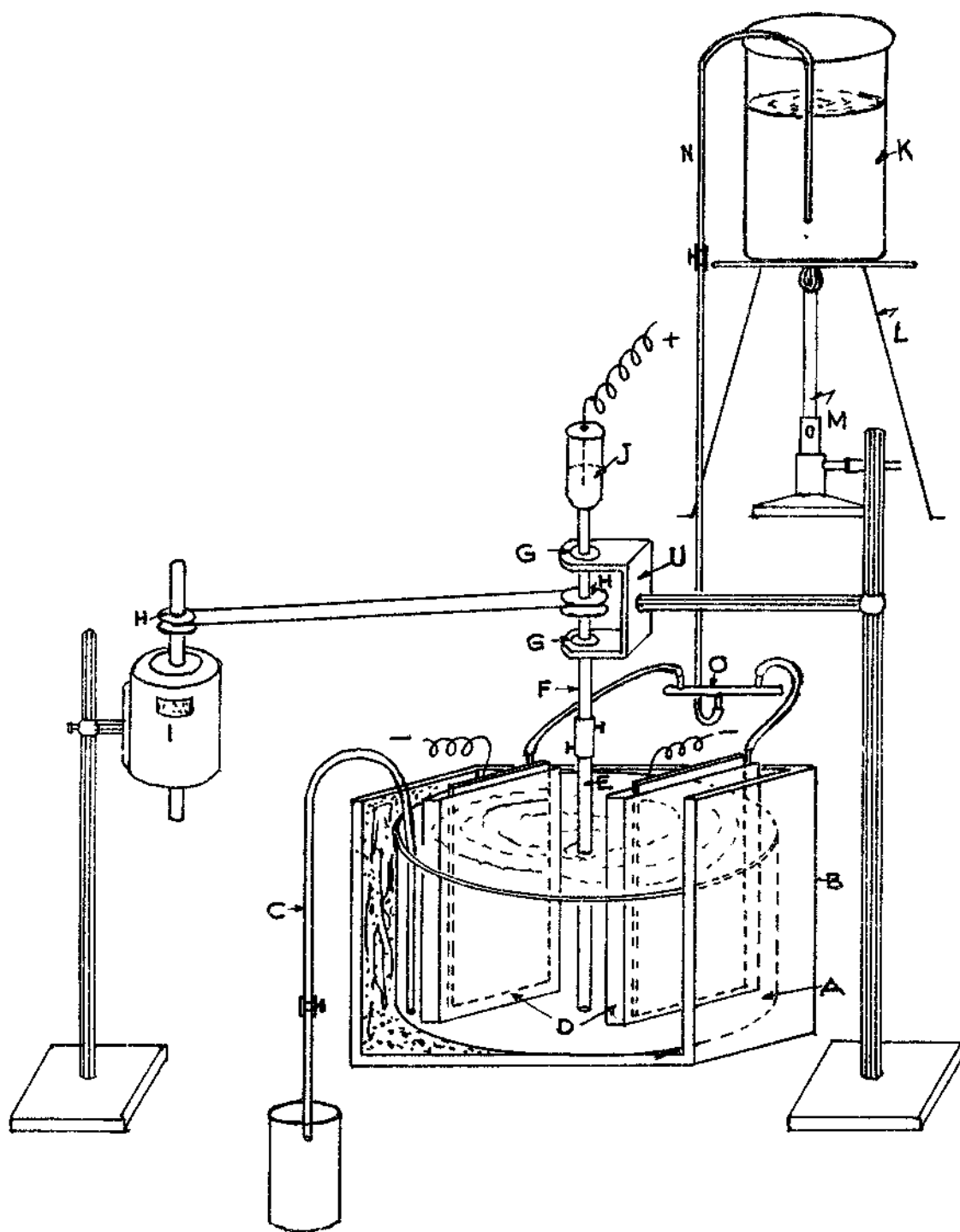


FIG. 1

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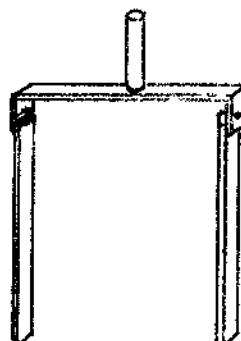
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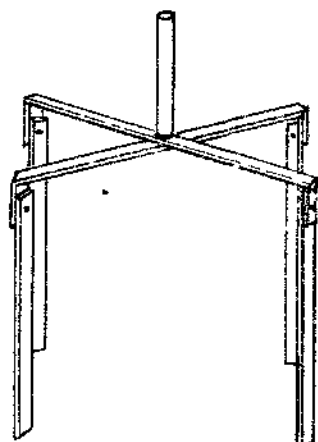
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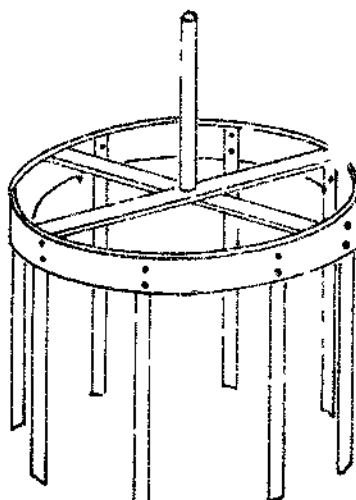
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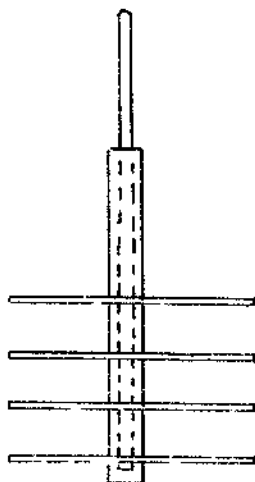
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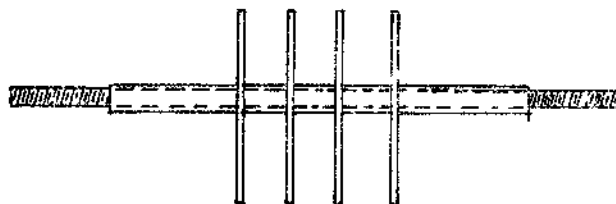
v



vi



vii



viii

FIG. 2

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TWO SHEETS
SHEET ONE

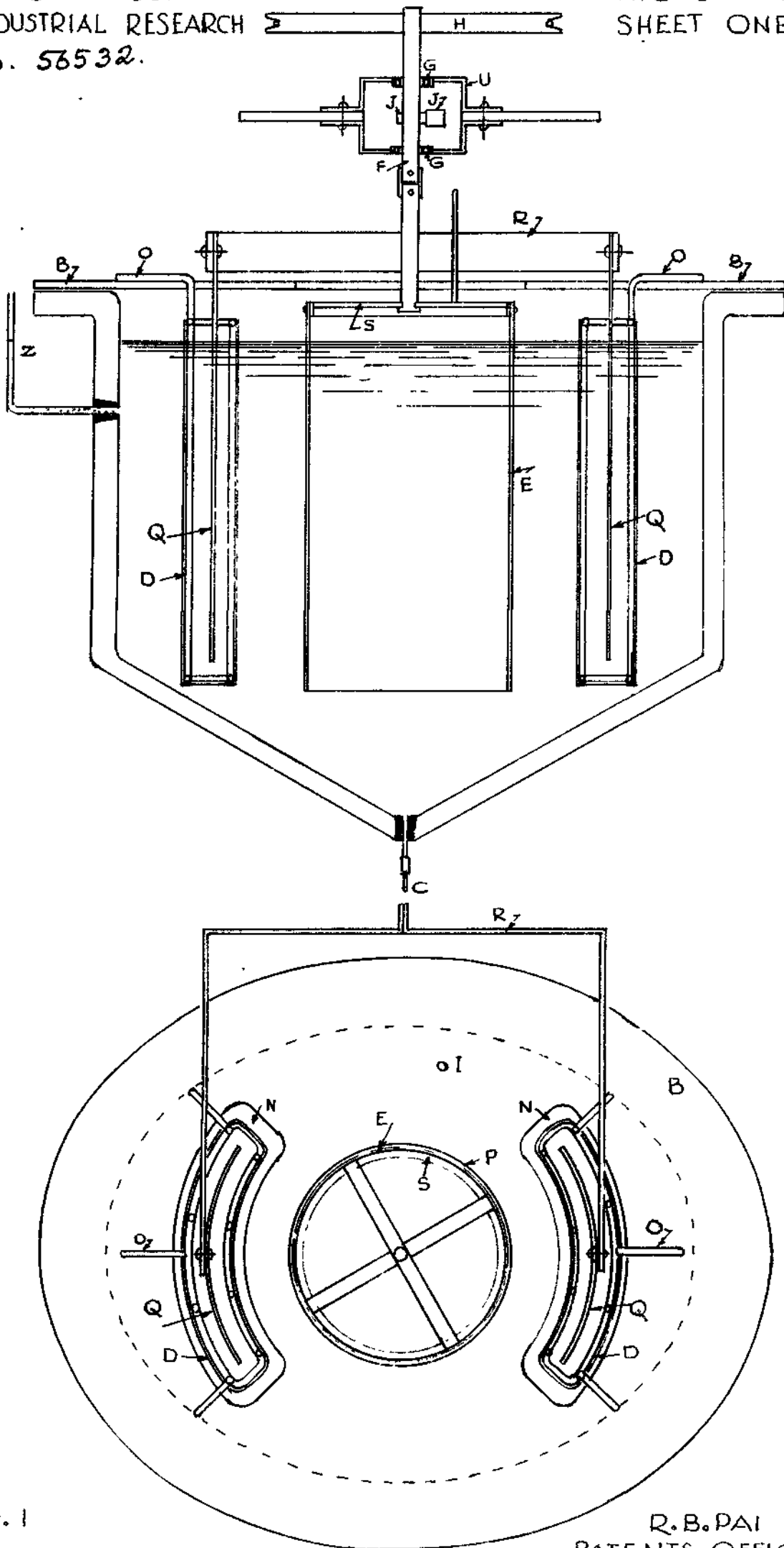


FIG. 1

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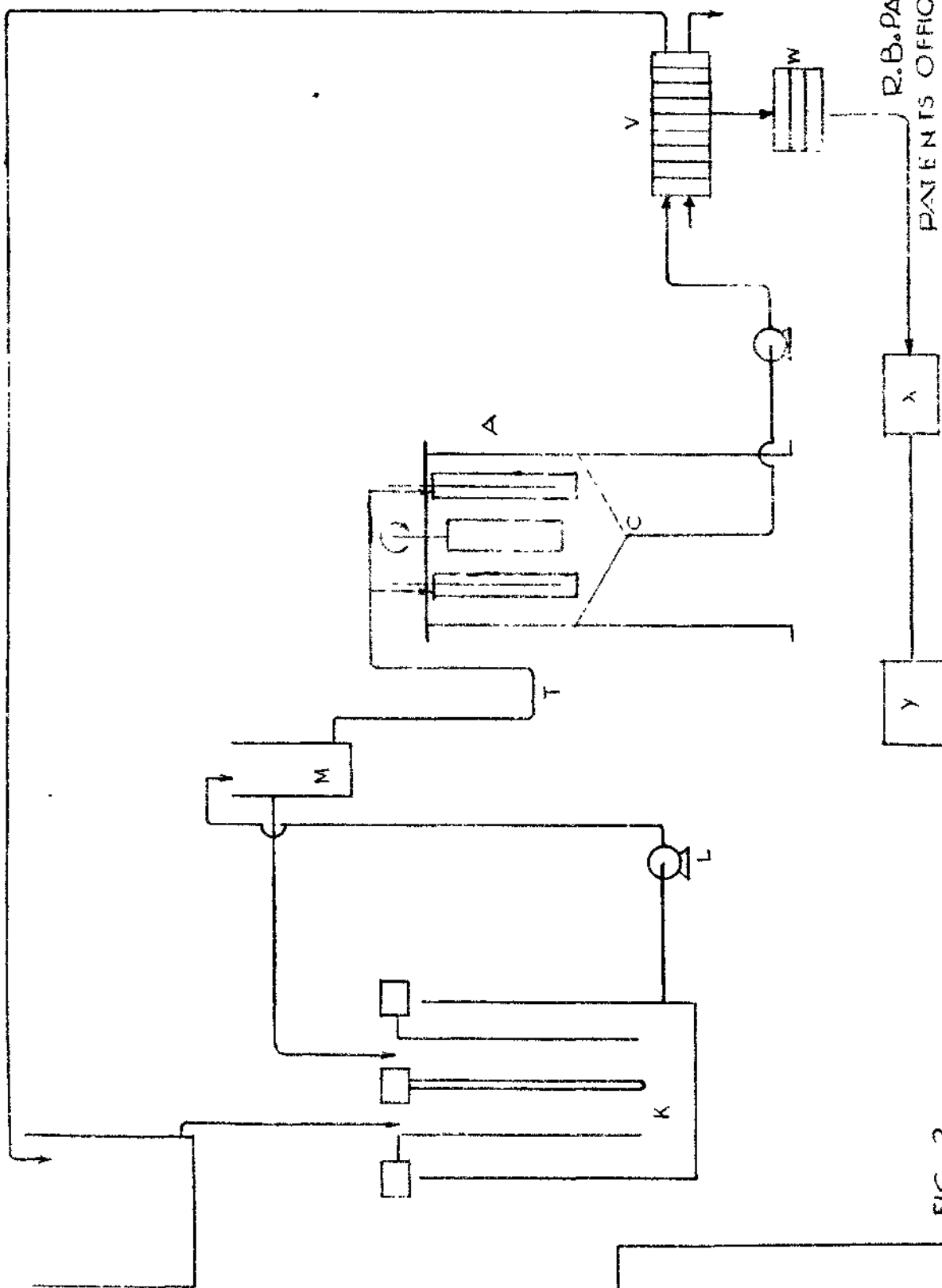


FIG 2

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