GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.
Specification No. 68869. Application No. 68869, dated 27th August 1959. Complete Specification left on 27th June 1960. (Application accepted 6th April 1961.)

PROVISIONAL SPECIFICATION

(Section No. 4)

" IMPROVEMENTS IN AND OR RELATING TO THE MANUFACTURE OF BENZIDINE AND SUBSTITUTED BENZIDINES. "

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, GOBICHETTIPALAYAM SRINIVASAN SUBRAMANIAN AND KODETHOOR SHRIVARA UDUPA, all of the Central Electro-chemical Research Institute India, all Indians.

Benzidines are an important class of intermediates in the dyestuff industries and are largely used in the synthesis of azo dyes, the most important member of which is Congo Red. In combination with heptaldehyde benzidine is used as an accelerator in rubber vulcanization. Benzidine also finds some application for detection of sulphates in water and the identification of blood.

The preparation of benzidine by the electrolytic reduction of a suspension of nitrobenzene in hot alkali has already been covered by an Indian Patent No. 32486 (1945). The conditions described therein are the use of stationary electrodes and low current densities with dissolved lead monoxide in the alkali. The present investigation has been directed to improve on the process and the improvements made now are (a) the use of a rotating cathode and (b) consequent employment of high current densities, maintaining high efficiency of reduction and also (c) lowering the total time of electrolysis using the same cathode area. The use of rotating cathode simplifies the design of high capacity cells. It is established that even high current densities are beneficial for good yields. The reduction is smooth and almost theoretical yields of hydrazo benzene is obtained. For the same amperage as could be passed in the previous patent (No. 32486), the present improvement made uses a more compact cell thereby leading to savings in floor space. We claim the rotation of the cathode as a novel feature of the invention leading to advantages enumerated above.

Procedure :

On a laboratory scale, the reduction was studied using a disc-type mild steel, nickel or nickel plated, metal (copper) cathode and 10% sodium hydroxide solution as catholyte and anolyte being 30% NaOH. A diaphragm of asbestos cloth was used in the form of a cylinder wound on a mild steel or nickel plated mild steel cage. The temperature of electrolysis was 80-85° and 100 g of nitrobenzene was added for every 400 cc of the catholyte and the reduction was carried out to the theoretical time based on nitrobenzene taken. When 90% of the current was passed, xylene was added and the reduction was completed when the colour of the xylene layer becomes almost of constant (light yellow) shade. The xylene layer was separated and converted to benzidine by standard methods of reacting with acids.

Experimental :

The cell consists of one litre spoutless pyrex beaker with a tight-fitting cover made of asbestos cement sheet (1/8" thick) with proper holes for asbestos diaphragm (2" diam. × 8" long), rotating cathode and condenser. 400 cc of 10% (by weight) sodium hydroxide was taken and to it was added 1% (weight : volume) of lead monoxide and the alkali heated till the temperature was 85°C. Lead monoxide dissolves while heating and the clear solution is taken into the cell. 100 cc of 30% sodium hydroxide (by weight) is also prepared as anolyte and separately heated to 85°C and taken in the anode compartment. The cathode is made of six mild steel discs 1" diam. with 5 spacers mounted on a shaft and the total cathode area is nearly 0.8 sq. dm². It is rotated by a fractional horse power motor through a glass bush at 1800-2000 R.P.M. The anode is a strip of mild steel plate or of nickel plated copper, 1/8" thick. Current density of the order of 15 to 25 amp/dm² was employed. Nitrobenzene in the ratio of 100 g : 400 cc of catholyte was added. When 90% of the theoretical current was passed, xylene is added (100 cc for every 100 g of nitrobenzene) and the electrolysis carried to the theoretical time when it is found that the xylene layer assumes a colour of constant shade.

The xylene layer is then separated and converted to benzidine with hydrochloric acid and ice and the benzidine hydrochloride is crystallised and the yield is calculated as hydrazobenzene.

The yields obtained are 88 to 90% of hydrazo-benzene and the results were confirmed by a number of laboratory experiments.

EXAMPLE I

Catholyte	:	400 cc of 10% NaOH
PbO	:	4 gms
Anolyte	:	100 cc of 30% NaOH
Weight of nitrobenzene taken	:	100 g
Cathode	:	Disc type iron
Area	:	0.8 sq. dm
Current density	:	25 amp/dm²
Time	:	Theoretical current
Temperature	:	80 to 85°C
Benzidine hydrochloride obtained	:	78.7 gms
Theoretical yield	:	89.43 gms
% yield	:	$\frac{78.7}{89.43} \times 100$
		=88%

EXAMPLE II

Catholyte	:	400 cc of 10% NaOH
PbO	:	4 gms
Anolyte	:	100 cc of 30% NaOH
Weight of O-nitrotoluene taken	:	100 g
Cathode	:	Disc type iron
Area	:	0.8 sq. dm
Current density	:	25 amp/dm²
Time	:	Theoretical current
Temperature	:	80 to 85°C
o-Tolidine sulphate obtained	:	42.32 gms
Theoretical yield	:	103.04
% yield		37.41%
%yield of Azo toluene		28.75%
%yield of o-Toludine		11.5%

Price: TWO RUPEES.

According to our invention, the rotating cathode is used for the reduction and is best made by mild steel in the form of discs with a coating of spongy lead obtained in situ by addition of 1% (weight : volume) of lead monoxide to the catholyte, so that spongy lead deposited amounts to above 0.014 mole/dm². The cathode employed could be also cylindrical shaped mild steel, or made of nickel or nickel plated copper or other metals.

The results obtained on a large scale laboratory unit will be reported in the complete specification to be filed later.

The following are the outstanding features of the present invention :

(1) A process for the electrolytic reduction of nitrobenzene and substituted nitrobenzenes is characterised by the use of a rotating cathode enabling use of a wide range of current density of the order of 3 to 30 amp/dm², but preferably high current density of the order of 15 to 25 amp/dm².

(2) A process as in (1) wherein, either mild steel, nickel or nickel plated metal (copper) are used as cathodes and mild steel, nickel or nickel plated metals (copper) are used as anodes.

(3) A process as in (1) wherein reduction is carried out by keeping nitrobenzene in suspension in caustic alkali solution of 5 to 15% strength but preferably in alkali of 10% strength.

(4) A process as in (1) wherein lead monoxide is added to the catholyte so as to give a spongy cathodic deposit of lead, not less than 0.014 mole/dm².

(5) A process as above wherein the electrolysis is carried out at a temperature of 70°C to 95°C but preferably at 80° to 85°C.

(6) A process as above wherein a solvent such as xylene, toluene etc., is added when 90% of the theoretical current has been passed to help keep the hydrazo-benzene in solution.

(7) A process as above wherein a diaphragm of asbestos cloth over a mild steel, nickel or nickel plated metal cage is empolyed to from the anode chamber.

(8) A process as in (1) wherein the use of rotating cathode permits easy design of high capacity cells requiring less floor space, etc.

R. BHASKAR PAI
Patents Officer,
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

Dated this 20th day of August, 1959.

COMPLETE SPECIFICATION

(Section 4)

Specification No. 68869.

" IMPROVEMENTS IN AND OR RELATING TO THE MANUFACTURE OF BENZIDINE AND SUBSTITUTED BENZIDINES. "

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, GOBICHETTIPALAYAM SRINIVASAN SUBRAMANIAN AND KODETHOOR SHRIVARA UDUPA, all of the Central Electro-chemical Research Institute, India, all Indians.

Benzidines are an important class of intermediates in the dyestuff industries and are largely used in the synthesis of azo dyes, the most important member of which is Congo Red. In combination with heptaldehyde benzidine is used as an accelerator in rubber vulcanization. Benzidine also finds some application for detection of sulphates in water and the identification of blood.

The preparation of benzidine by the electrolytic reduction of a suspension of nitrobenzene in hot alkali has already been covered by an Indian Patent No. 32486 (1945). The conditions described therein are the use of stationary electrodes and low current densities with dissolved lead monoxide in the alkali.

The invented process for the manufacture of benzidines and substituted benzidines by the electrolytic reduction of nitrobenzenes or nitrobenzenes substituted with $-CH_3$, $-C_2H_5$, $-OCH_3$, $-OC_2H_5$, Cl, -OH groups in ortho position to $-NO_2$ group and reacting the hydrazobenzenes and substituted hydrazobenzenes thus obtained with acid is characterized in that the electrolytic reduction is carried out in presence of a rotating cathode at a current density of 3-50 amps/dm², preferably, 15-40 amps/dm², under alkaline conditions at a temperature above 70°C with deposition of spongy lead on the cathode.

The present investigation has been directed to improve on the process and the improvements made now are (a) the use of a rotating cathode and (b) consequent employment of high current densities, maintaining high efficiency of reduction and also (c) lowering the total time of electrolysis using the same cathode area. The use of rotating cathode simplifies the design of high capacity cells whereas for a corresponding amperage to be passed under stationary electrode condition, the cells will have to be bigger occupying a larger space. For example the cells described in Indian Patent No. 32486 (1945) will handle 40 litres of alkali and 10 kg of nitrobenzene and can be operated with 400-450 amps only. For the same amount of alkali and nitrobenzene with the cells of the present patent, 1000 amps could be passed so that the reduction is over 18 hours earlier ; or for the same duration of electrolysis is possible in the previous cells (India Patent 32486 (1945), 2½ times the quantity of benzidine could be obtained with the rotating cathode cell. In other words, the capacity of the present cells with rotating cathode is two and a half times the capacity of the corresponding sized cells described in Indian Patent 32486. The use of rotating cathode, therefore, simplifies the design of high capacity cells. It is established that even high current densities are beneficial for good yields. The reduction is smooth and almost theoretical yields of hydrazobenzene is obtained. For the same amperage as could be passed in the previous Patent (No. 32486), the present improvement enables the use of a more compact cell thereby leading to savings in floor space. Thus, the process enables the use of high capacity cells (nearly 2½ times the capacity of cells using stationary cathode), requiring, therefore, less floor space than what is required for the same capacity cells using stationary cathode. We claim the rotation of the cathode as a novel feature of the invention leading to advantages enumerated above.

Procedure :

On a laboratory scale, the reduction was studied using a disc-type mild steel, nickel or nickel plated metal (copper) cathode having a deposit of spongy lead as described in the examples given

hereinbelow and 10% sodium hydroxide solution as catholyte and anolyte being 30% NaOH. A diaphragm of asbestos cloth was used in the form of a cylinder wound on a mild steel, stainless steel or nickel-plated mild steel cage. The temperature of electrolysis was 80-85° and 100 g of nitrobenzene was added for every 400 cc of the catholyte and the reduction was carried out to the theoretical time based on nitrobenzene taken. When 90% of the current was passed, xylene was added and the reduction was completed when the colour of the xylene layer becomes almost of constant (light yellow) shade. The xylene layer was separated and converted to benzidine by standard methods of reacting with acids.

Experimental :

The cell consists of one litre spoutless pyrex beaker with a tight-fitting cover made of asbestos cement sheet (1/8" thick) with proper holes for asbestos diaphragm (2" diam. × 8" long), rotating cathode and condenser. 400 cc of 10% (by weight) sodium hydroxide was taken and to it was added 1% (weight: volume) of lead monoxide and the alkali heated till the temperature was 85°C. Lead monoxide dissolves while heating and the clear solution is taken into the cell. 100 cc of 30% sodium hydroxide (by weight) is also prepared as anolyte and separately heated to 85°C and taken in the anode compartment. The cathode is made of six mild steel discs 1" diam. with 5 spacers mounted on a shaft and the total cathode area is nearly 0.8 sq. dm. It is rotated by a fractional horse power motor through a glass bush at 1800-2000 R.P.M. The anode is a strip of mild steel plate or of nickel plated copper or stainless steel plate, 1/8" thick. Current density of the order of 15 to 25 amp/dm² was employed. Nitrobenzene in the ratio of 100 g : 400 cc of catholyte was added. When 90% of the theoretical current was passed, xylene is added (100 cc for every 100 g of nitrobenzene) and the electrolysis carried to the theoretical time when it is found that the xylene layer assumes a colour of constant shade.

The xylene layer is then separated and converted to benzidine with hydrochloric acid and ice and the benzidine hydrochloride is crystallised and the yield is calculated as hydrazobenzene.

The yields obtained are 88 to 90% of hydrazobenzene and the results were confirmed by a number of laboratory experiments :

EXAMPLE I

Preparation of hydrazobenzene and benzidine

Catholyte	: 400 cc of 10% NaOH
PbO	: 4 g
Anolyte	: 100 cc of 30% NaOH
Weight of nitrobenzene taken	: 100 g
Cathode	: Disc type iron
Area	: 0.8 sq. dm.
Current density	: 25 amp./sq dm.
Time	: Theoretical current
Temperature	: 80 to 85° C
Benzidine hydrochloride obtained	: 78.7 g
Theoretical yield	: 89.4 g
°/₀ %yield	: 88

EXAMPLE II

Preparation of Tolidine

Catholyte	: 400 cc of 10% NaOH
PbO	: 4 g
Anolyte	: 100 cc of 30% NaOH
Weight of O-nitro-toluene taken	: 40 g
Cathode	: Disc type iron
Area	: 0.8 sq. dm.
Current density	: 20 amp./sq. dm.
Time	: Theoretical current
Temperature	: 80 to 85°C.
o-Tolidine hydrochloride obtained	: 18.4 g
Theoretical yield	: 36.3 g
°/₀ %yield	: 50.8
%yield of Azo tolune	: 23.0
%yield O-Toludine	: 12.9

EXAMPLE III

Preparation of dichlorobenzidine

Catholyte	: 400 cc of 10% NaOH
PbO	: 4 g
Anolyte	: 100 cc of 30% NaOH
Weight of O-nitrochlorobenzene taken	: 100 g
Cathode	: Disc type iron
Area	: 0.8 sq dm.
Current density	: 25 amp./sq. dm.
Time	: Theoretical current
Temperature	: 80 to 85°C.
2-2′ dichloro hydrazobenzene	: 66 g.
Theoretical yield	: 80.3 g.
°/₀ %yield	: 82.2
%yield of o-chloraniline	: 9.8

EXAMPLE IV

Preparation of Dianisidine :

Catholyte	: 400 cc of 10% NaOH
PbO	: 4 g.
Anolyte	: 100 cc of 30% NaOH
Weight of O-Nitro anisole	: 100 g.
Cathode	: Disc type iron
Area	: 0.8 Sq. dm.
Current density	: 25 amp./dm.
Time	: Theoretical Current
Temperature	: 80 to 85°C.
Yield of Dianisidine	: 29.7 g.
Theoretical yield	: 39.9 g.
%Yield Dianisidine	: 74 5
%Yield of azoanisole	: 20.5
%Yield of Anisidine	: 5.8

Large scale preparation of Benzidine : The invention will now be described with the help of accompanying drawings wherein Fig. 1 shows the elevation and Fig. 2 the plan of the large scale cell.

The cell consists of a concrete vessel (A) (8" inside diameter and 1" thick and depth of 10"). It is fitted with a wooden cover (B) having the necessary openings for the rotating cathode (C), Asbestos diaphragms (E), Condenser (F) thermometer (G). The Diaphragm is made of a nickel plated iron cage in the form of a rectangle (1" x 4 x 12") on which is wound the asbestos cloth. The cathode is of m.s. consisting of 3" × 1/8" Discs. The discs are welded at a distance of 1" on an iron tube (C_1) (3/4" dia steam pipe) into which is jammed a copper rod (C_2) so that the current is carried through the copper. There are 6 discs welded on the cathode which is rotated by a 1 H.P. motor at a speed of 1800 r.p.m. Electrical contacts are given through a mercury cup. The anodes (D)

consist of 1/2″ copper rod inserted tight into an iron tube to which is welded two nickel-plated M.S. strips 1″ × 10″ × 1/8″. The cell is also provided with cold fingers (H) made out of glass tube of 1-1/2″ outside diameter × 12″ long with a 1/2″ dia., glass tube for the inlet and outlet (for cooling the cell).

EXAMPLE V

Catholyte	:	4 litres of 10% NaOH
PbO	:	40 g.
Anolyte	:	1 litre of 30% NaOH
Weight of nitrobenzene taken	:	1000 g.
Cathode	:	Disc-type iron.
Area	:	5.89 dm².
Current density	:	30 amps./sq. dm.
Temperature	:	80 to 85°C.
%Yield of Benzidine	:	80
%Yield of azobenzene	:	7.3
%Yield of aniline	:	6.1

Reuse of alkali: Experiments were run using the same alkali after making up to 10%. The results are given below :-

		Yield of benzidine (%)	Yield of azo benzene (%)	Yield of aniline (%)
2nd use		82.4	12.7	2.1
3rd use		81.3	12.3	3.1
4th use		80.8	11.7	3.4
5th use, 6th use, 7th use, 8th use	av.	81	10.4	4.5

According to our invention, the rotating cathode is used for the reduction and is best made by mild steel in the form of discs with a coating of spongy lead obtained in situ by addition of 1% (weight : volume) of lead monoxide to the catholyte, so that spongy lead deposited amounts to about 0.014 mole/dm². The cathode employed could also be cylindrical shaped mild steel, or made of nickel or nickel-plated copper or other metals.

The results obtained on a large scale laboratory unit are reported above.

We Claim :—

1. A process for the manufacture of benzidines and substituted benzidines which consists in the electrolytic reduction of nitrobenzenes or nitrobenzenes substituted with $-CH_3$, $-C_2H_5$, $-OCH_3$, $-OC_2H_5$, Cl, -OH groups in ortho position to $-NO^2$ group and reacting the hydrazobenes and substituted hydrazobenzenes thus obtained with acid which is characterised in that the electrolytic reduction is carried out in presence of a rotating cathode at a current density of 3-50 amps/dm², preferably, 15-40 amps/dm², under alkaline conditions at a temperature above 70°C with deposition of spongy lead on the cathode.

2. A process as claimed in (1) wherein, either mild steel, nickel or nickel plated metal are used as cathodes and mild steel, stainless steel, nickel or nickel plated metals are used as anodes.

3. A process as claimed in claim (1) wherein reduction is carried out by keeping nitrobenzene in suspension in caustic alkali solution of 5 to 15% strength but preferably in alkali of 10% strength.

4. A process as claimed above wherein, the same alkali is reused in subsequent reductions without affecting the efficiency of reduction.

5. A process as claimed in claim (1) wherein lead monoxide is added to the catholyte so as to give a spongy cathodic deposit of lead, on rotating cathode, not less than 0.014 mole/dm².

6. A process as claimed above wherein the electrolysis is carried out at a temperature of 70°C. to 95°C. but preferably at 80°C. to 85°C.

7. A process as claimed in any of the above claims wherein a solvent such as xylene or toluene is added when 90% of the theoretical current has been passed to help keep the hydrazobenzene in solution.

8. A process as claimed in any of the above claims wherein a diaphragm of asbestos cloth over a mild steel, stainless steel, nickel or nickel plated metal cage is employed to form the anode chamber.

9. A process as claimed above wherein the disc-type cathode consists of a copper rod fitted into a m.s. pipe carrying the discs so that the current carrying capacity of the cathode is increased.

10. A process as claimed in claim (1) wherein high capacity cells (nearly 2½ times the capacity of cells using stationary cathode), requiring, therefore, less floor space than what is required for the same capacity cells using stationary cathode are employed.

11. A process for the manufacture of benzidine and substituted benzidines as described above and claimed in the preceding claims.

R. Bhaskar Pai,
Patents Officer,
Council of Scientific & Industrial Research.

Dated this 24th day of June, 1960.

Printed by The Nolys Printing Works, Calcutta-1.

COUNCIL OF SCIENTIFIC AND
INDUSTRIAL RESEARCH

No. 68869.

NUMBER OF SHEET ONE

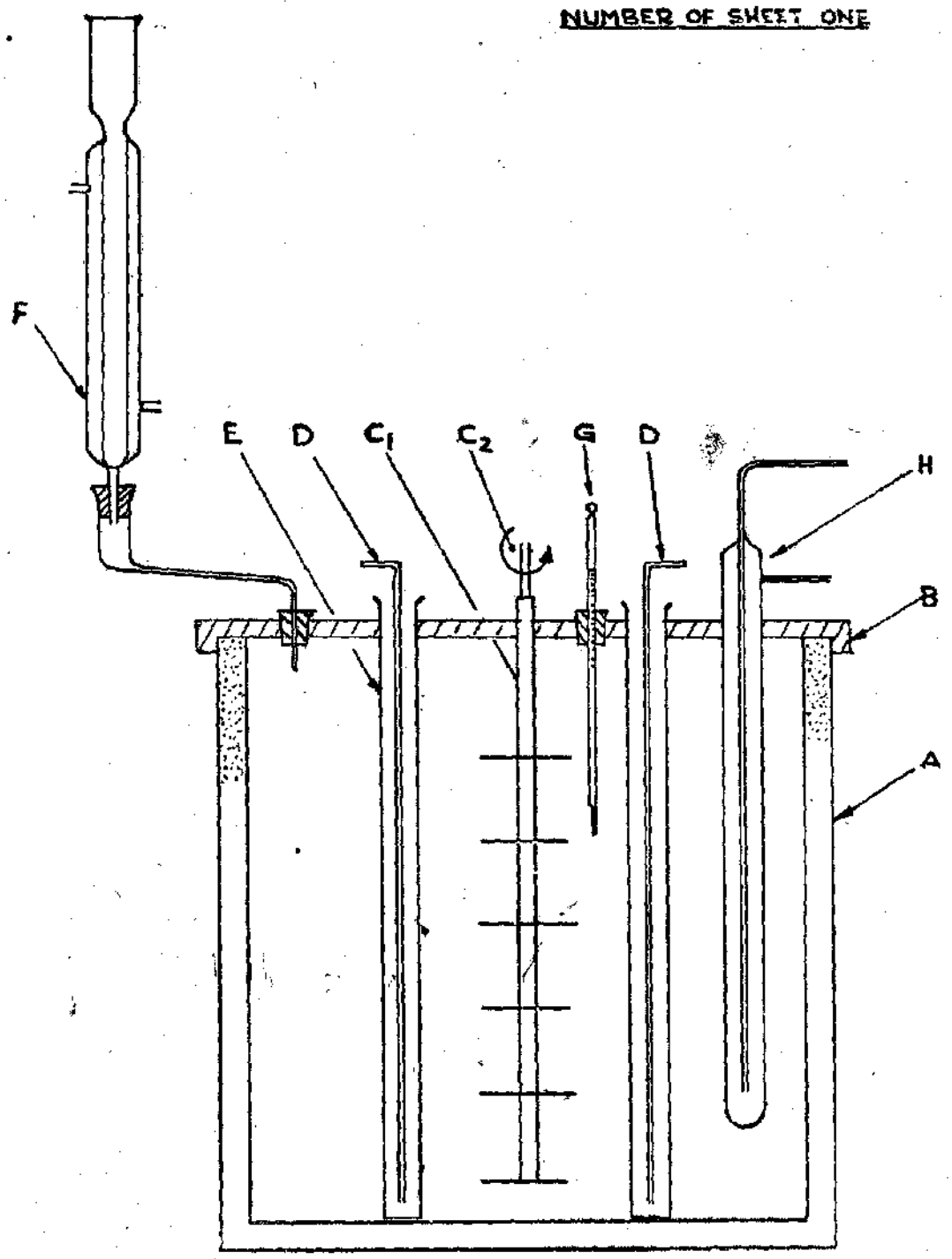

Fig 1

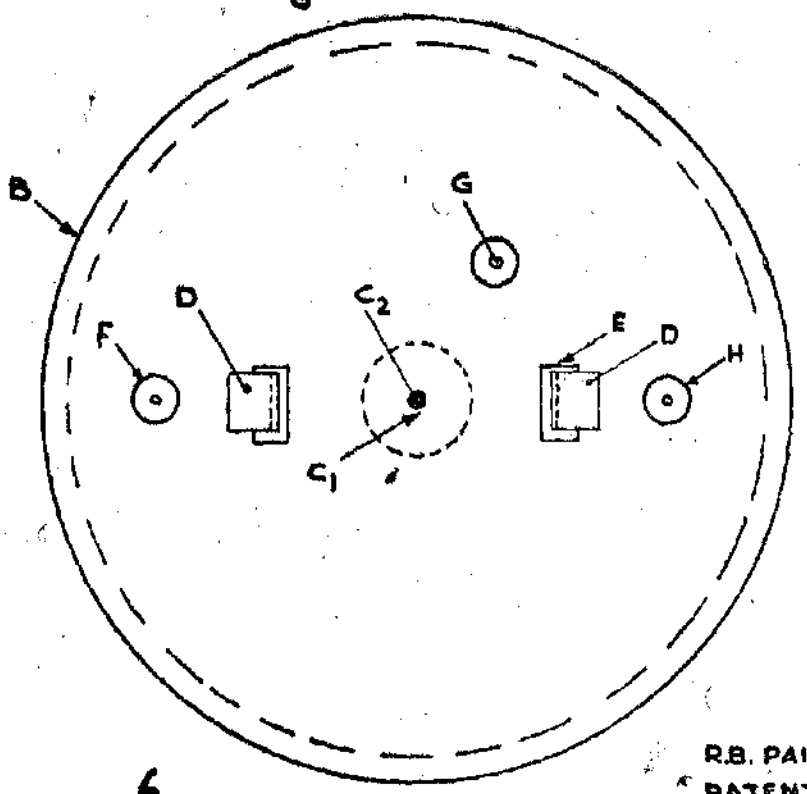

Fig. 2

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R.B. PAI,
PATENTS OFFICER
C.S.I.R.