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Index at acceptance—32F 2a[IX(1)]; 70C7[LVIII(5)]

"IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC REDUCTION OF 3-NITRO-p-CRESOL TO 3-AMINO-p-CRESOL

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI-1 INDIA, AN INDIAN REGISTERED BODY INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

This is an invention by Handady Venkatakrishna Udupa, Gobichettipalayam Srinivasan Subramanian and Payyalur Narayanan Anantharaman, all Indians, all of Central Electrochemical Research Institute, Karaikudi.

PROVISIONAL

The following Specification describes the nature of this invention.

This invention relates to improvements in or relating to the electrolytic reduction of 3-nitro-p-cresol to 3-amino-p-cresol.

Hitherto it has been proposed to reduce 3-nitro-p-cresol by chemical methods using iron and hydrochloric acid or by electrochemical methods using stationary cathodes.

These are open to the objection in that the product isolation is made more difficult and purity and yield of the product are low. Moreover, the electrochemical method using stationary cathodes necessitated the use of solvent like ethyl alcohol to bring into solution the nitro compound for smooth reduction. The other disadvantage of this technique is that only low current densities were employed. A maximum efficiency of 55.6% is reported at a current density of 6 amp/dm^2.

The object of this invention is to obviate these disadantages by reducing 3-nitro-p-cresol electrochemically using the rotating cathode technique. By this technique the use of a solvent is avoided and the reduction is possible with good current efficiencies even at high current densities.

To these ends, the invention broadly consists in reducing a suspension of 3-intro-p-cresol in a catholyte of sulphuric acid or sodium sulphate but preferably the former, up to a concentration of 10% by volume, using a rotating cathode of copper, zinc or tin but preferably copper in a divided cell. The reduction is further carried out at temperatures up to 70°C using a range of current density up to 40 amp/dm^2 but preferably at 10 amp/dm^2. The anolyte is dilute sulphuric acid up to 30% strength and a ceramic porous pot is used as a diaphragm with lead anode. After the reduction is over, the catholyte is steam distilled to recover any unreduced nitro compound and then neutralised with alkali such as ammonia, caustic soda or washing soda up to pH 7 when the 3 amino-p-cresol separates out. It is filtered and recrystallised from boiling water. The purity was found to be 100% and has been found suitable by a consumer firm.

Alternately, the catholyte is vacuum concentrated and the product isolated as sulphate so that the balance free acid along with make up sulphuric acid is reused as catholyte.

The following typical examples are given to illustrate the invention :

EXAMPLE I

Catholyte :	300 ml of 10% sulphuric acid
Cathode :	Rotating disc-type copper—Area=0.7 dm^2
Nitrocompound taken :	20 g.
Temperature of reduction :	60-70°C
Anolyte :	50 ml of 20% sulphuric acid
Anode :	Lead
Diaphragm :	Unglazed porous ceramic pot.
Cathode current density :	10 amp/dm^2
Current :	7 amps
Cell voltage :	5.0 volts
Duration :	3.5 hours
Weight of 3-amino-p-cresol :	12.7 g. Theoretical : 16.08 g.
Nitrocompound recovered :	1.2 g.
Current efficiency :	79%
% yield of 3-amino-p-cresol :	94%
Energy consumption :	8.1 kwh/kg.

EXAMPLE II

Catholyte :	300 ml of 10% sulphuric acid.
Cathode :	Rotating disc-type copper—Area=0.7 dm^2
Nitrocompound taken :	20 g.
Temperature of reduction :	50-60°C
Anolyte :	50 ml of 30% sulphuric acid.
Anode :	Lead
Diaphragm :	Unglazed porous ceramic pot.
Currant density :	15 amp/dm^2
Current :	10.5 amps
Duration :	2.5 hours
Cell voltage :	5.0 volts
Weight of 3-amino-p-cresol :	13.5 g. Theoretical : 16.08 g.
Nitrocompound recovered :	3.1 g.
Current efficiency :	83.95 %
% yield of 3-amino-p-cresol :	85%
Energy consumption :	8.7 kwh/kg.

The following are the main advantages of the invention :

1) The reduction efficiency is high and the use of a solvent is avoided as a result of rotating cathode technique and product isolation is thereby simplified.

2) The product of high purity is obtained without contamination with iron compounds as in the case of chemical reduction process using iron powder and acid.

3) Design of high amperage cells for the process is possible on account of the successful results obtained by the rotating cathode technique.

4) The product can be isolated as a free base in the present process by direct neutralization of the catholyte, whereas if solvents are used they would interfere with the isolation of the product.

5) The product can be isolated as the sulphate by carrying out a distillation of the catholyte under reduced pressure and cooling and the free base liberated as usual from the sulphate.

6) The catholyte, after isolation of the product as sulphate, can be diluted and reused in the process by making up the sulphuric acid content.

Price : TWO RUPEES.

COMPLETE

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

The invention relates to the electrolytic reduction of 3-nitro-p-cresol to 3-amino-p-cresol, the latter being useful as an intermediate in the dyestuff industry as the intermediate.

Hitherto it has been proposed to reduce 3-nitro-p-cresol by chemical methods using iron and hydrochloric acid or sometimes by electrochemical methods using stationary cathodes.

These are open to the objection in that the product isolation is made more difficult and the purity and yield of the product are low. Moreover the electrochemical method using stationary cathodes necessitated the use of a solvent like ethyl alcohol to bring into solution the nitro compound for smooth reduction and to avoid polarization. The other disadvantage of this technique is that only low current densities were employed. A maximum efficiency of 55.6% is reported at a current density of 6 amp/dm^2.

The main object of the invention; other objects if any :

The object of this invention is to obviate these disadvantages by reducing 3-nitro-p-cresol electrochemically using the rotating cathode technique. By this technique the use of a solvent is avoided and the reduction is possible with good current efficiencies even at high current densities. Scale-up of cell becomes easy and high amperage cells can be readily designed for the reduction.

The main finding (the new principie) underlying the invention :

The main finding of the invention is the electrolytic reduction of 3-nitro-p-cresol to 3-amino-p-cresol using the rotating electrode technique and having a suspension of the nitro compound thereby avoiding the use of a solvent.

The following are the main advantages of the invention :

(1) The reduction efficiency is high and the use of a solvent is avoided as a result of rotating cathode technique and product isolation is hereby simplified.

(2) The product of high purity is obtained without contamination with iron compounds as in the case of chemical reduction process using iron powder and acid.

(3) Design of high amperage cells for the process is posssible on account of the successful results obtained by the rotating cathode technique.

(4) The product can be isolated as a free base in the present process by direct neutralisation of the catholyte, whereas if solvents are used they would interfere with the isolation of the product.

(5) The product can be isolated as the sulphate by carrying out a distillation of the catholyte under reduced pressure and cooling and the free base liberated as usual from the sulphate.

(6) The catholyte, after isolation of the product as sulphate, can be diluted and reused in the process by making up the sulphuric acid content.

To these ends the invention broadly consists in reducing a suspension of 3-nitro-p-cresol in a catholyte of sulphuric acid or sodium sulphate but preferably the former, up to a concentration of 10% by volume, using a rotating cathode of copper zinc or tin but preferably copper in a divided cell. The reduction is further carried out at temperatures up to 70°C using a range of current density up to 40 amp/dm^2 but preferably at 10 amp/dm^2—The anolyte is dilute sulphuric acid up to 30% strength and a ceramic porous pot is used as a diaphragm with lead anode. After the reduction is over the catholyte is steam distilled to recover any unreduced nitro compound and then neutralised with alkali such as ammonia, caustic soda or washing soda when the 3 amino p-cresol separates out. It is filtered and recrystallised from boiling water. The purity was found to be 100% and has been found suitable by a consumer firm.

Alternatively the catholyte is vacuum concentrated and the product isolated as sulphate so that the balance of free acid along with make up sulphuric acid is reused as catholyte.

The following typical examples are given to illustrate the invention :

EXAMPLE

Experiment No. I.

Area of copper cathode	:	2.94 sq. dm.
Current	:	50 amps.
Current density	:	17 amp/dm^2
Volume of catholyte	:	2.5 litres.
Strength of catholyte	:	10% H_2SO_4
Volume of anolyte	:	300 ml.
Strength of anolyte	:	Same strength as catholyte.
Temperature	:	60-65%
Wt of $CuSO_4$. 5 H_2O added	:	2.5 gms.
Cell voltage	:	6 volts.
Wt of 3-nitro-p-cresol taken	:	200 gms.
Wt of 3-nitro-p-cresol unreduced	:	62 gms.
Wt of 3-amino-p-cresol obtained	:	124 gms.
Current efficiency based on 3 amino-p-cresol obtained.	:	77%
Energy consumption.	:	6.75 kwh/kg of 3 nitro-p-cresol.

Experiment No. 2 :

Area of copper cathode	:	2.94 sq. dm.
Current	:	50 amps.
Current density	:	17 amp/dm^2
Volume of catholyte	:	2.5 litres.
Strength of catholyte	:	10% H_2SO_4
Volume of anolyte	:	300 ml.
Strength of anolyte	:	Same as catholyte.
Temperature	:	60-65%
Wt of $CuSO_4$.5 H_2O added	:	2.5 gms.
Cell voltage	:	6 volts.
Wt of 3-nitro p cresol taken	:	200 gms.
Wt of 3-nitro p cresol unreduced	:	37.2 gms.
Wt of 3 amino-p-cresol obtained	:	110 gms.
Cell voltage	:	7.5 volts
Current efficiency based on 3 amino p cresol obtained	:	74.6%
Energy consumption	:	8.44 kwh/kg of 3 nitro-p-cresol

Experiment No. 3 :

Area of copper cathode	:	2.94 dq.dm.
Current	:	50 amps.
Current density	:	17 amp/dm^2
Volume of catholyte	:	2.5 litres.
Strength of catholyte	:	10% H_2SO_4
Volume of anolyte	:	300 ml.
Strength of anolyte	:	Same strength as catholyte.
Temperature	:	60-65°C
Wt of $CuSO_4$.5H_2O added	:	2.5 gms.
Cell voltage	:	9.5 volts.
Wt of 3-nitro p cresol taken	:	200 gms.
Wt of 3-nitro p cresol unreduced	:	25 gms.
Wt of 3-amino-p-cresol obtained	:	100 gms.
Current efficiency based on 3-amino p cresol obtained	:	62.2%
Energy consumption	:	10.7 kwk/kg of 3 nitro-p-cresol.
Overall yield of 3-amino-p-cresol	:	73.4%

Other new findings :

Addition of 0·1% $CuSO_4$ increases the efficiency of reduction.

The present invention consists of a process for the manufacture of 3-amino p cresol starting from 3 nitro p-cresol which comprises electrolytic reduction of the latter to the former wherein rotating cathode technique is employed.

Detailed description with reference to accompanying drawings.

Fig. 1. shows the general arrangement for carrying out the invention. The cell consists of a jacketted glass-lined m.s. tank (6) in which rotates a disc type cathode (2). Two ceramic porous pots (5) serve as diaphragms and lead is used as anode material. A condenser (1) is provided through which cold water is circulated. The temperature is measured by the thermometer (3).

Summary (Critical discussion) :

The invention broadly consists in reducing a suspension of 3 nitro p cresol in a catholyte of sulphuric acid or sodium sulphate but preferably the former upto a concentration of 10% by volume using a rotating cathode of copper, zinc or tin but preferably copper in a divided cell. The reduction is further carried out at temperatures up to 70°C using a range of current density up to 40 amp/dm^2 but preferably at 10 amp/dm^2. The anolyte is dilute sulphuric acid up to 30% strength and a ceramic porous pot is used as a diaphragm with lead or lead alloy anode. After the reduction is over the catholyte is steam distilled to recover any unreduced nitro compound and then neutralised with alkali such as ammonia, caustic soda or washing soda when the 3 amino p cresol separates out. It is filtered and recrystallised from boiling water. The purity was found to be 100% and has been found suitable by a consumer firm.

Alternatively, the catholyte is vacuum concentrated and the product isolated as sulphate so that the balance free acid along with make up sulphuric acid is reused as catholyte.

We claim :

1. A process for the electrochemical reduction of 3 nitro p-cresol to 3 amino p-cresol by taking the former as a suspension in sulphuric acid or sodium sulphate solution, preferably 10% strength and reducing at a rotating cathode at elevated temperatures up to 80°C using high current densities up to 40 amp/dm^2 and recovering the 3 amino p-cresol sulphate by concentrating the electrolyte under reduced pressure and cooling the same and re-using the mother liquor a number of times but not less than 3 times.
2. A process as claimed in claim (1) wherein when sulphuric acid bath is used, the 3 amino p cresol sulphate is recovered by concentrating the electrolyte under reduced pressure after removing the 3 nitro p cresol by steam distillation and filtering and reusing the filtrate for further electrolysis.
3. A process as in claim (1) wherein when sodium sulphate bath is used the 3 amino p cresol is recovered by neutralising the electrolyte with dilute acid preferably from anolyte and recovering the free base.
4. A process as claimed in any of the above claims in which the reduction is carried out using high current densities preferably up to 20 amp/dm^2.
5. A process as in any of the above claims in which reduction is carried out at elevated temperatures but preferably up to 50-60°C.
6. A process as claimed in any of the preceding claims wherein reduction is carried out in any of the anolyte but containing copper sulphate preferably 0.1% as addition agent.
7. A process as claimed in any of the above claims in which the reduction is carried out in a cell containing a porous diaphragm in which sulphuric acid or sodium sulphate solution, preferably 10% strength is taken and having an anode preferably of lead, lead silver or lead antimony alloy.
8. A process as claimed any of the above claims for making 3 amino p cresol as substantially hereinbefore described.

Dated this 16th day of March 1968.

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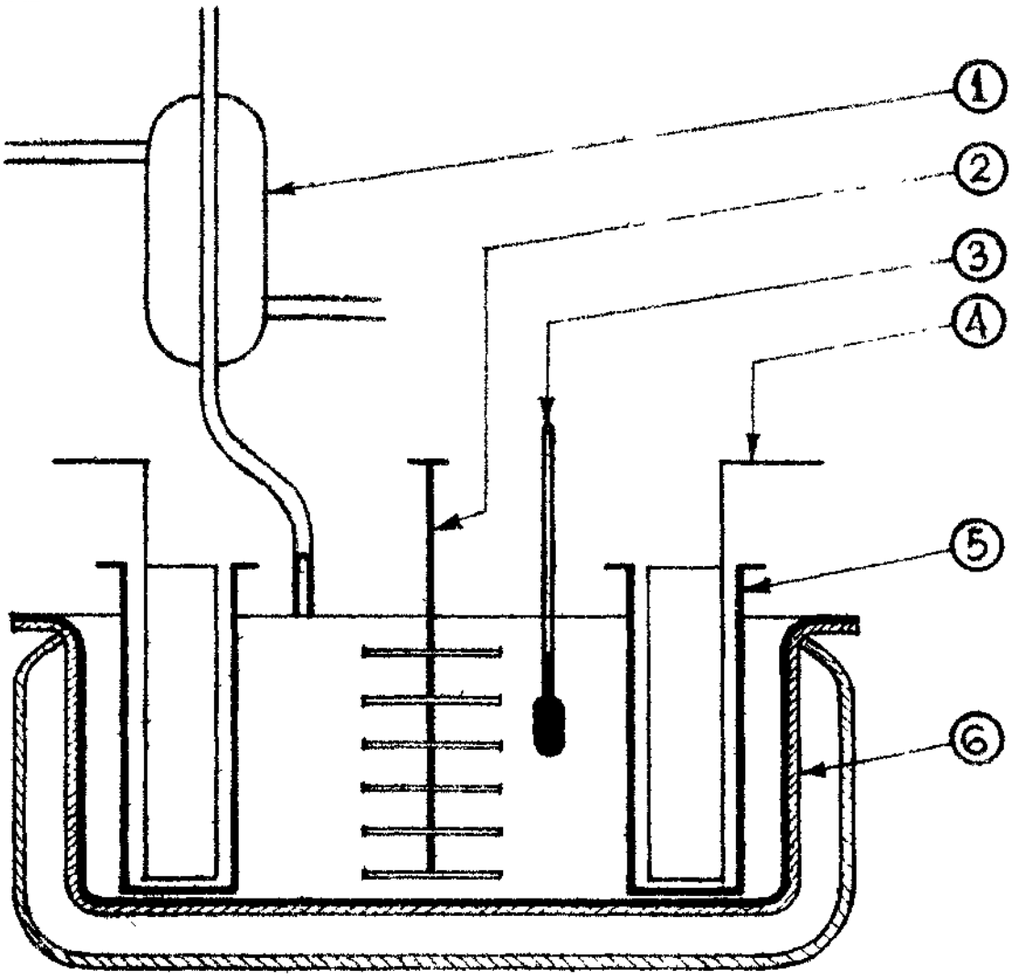

FIG. 1.

R B Pai

(R.B. PAI)
PATENTS OFFICER
C.S.I.R.

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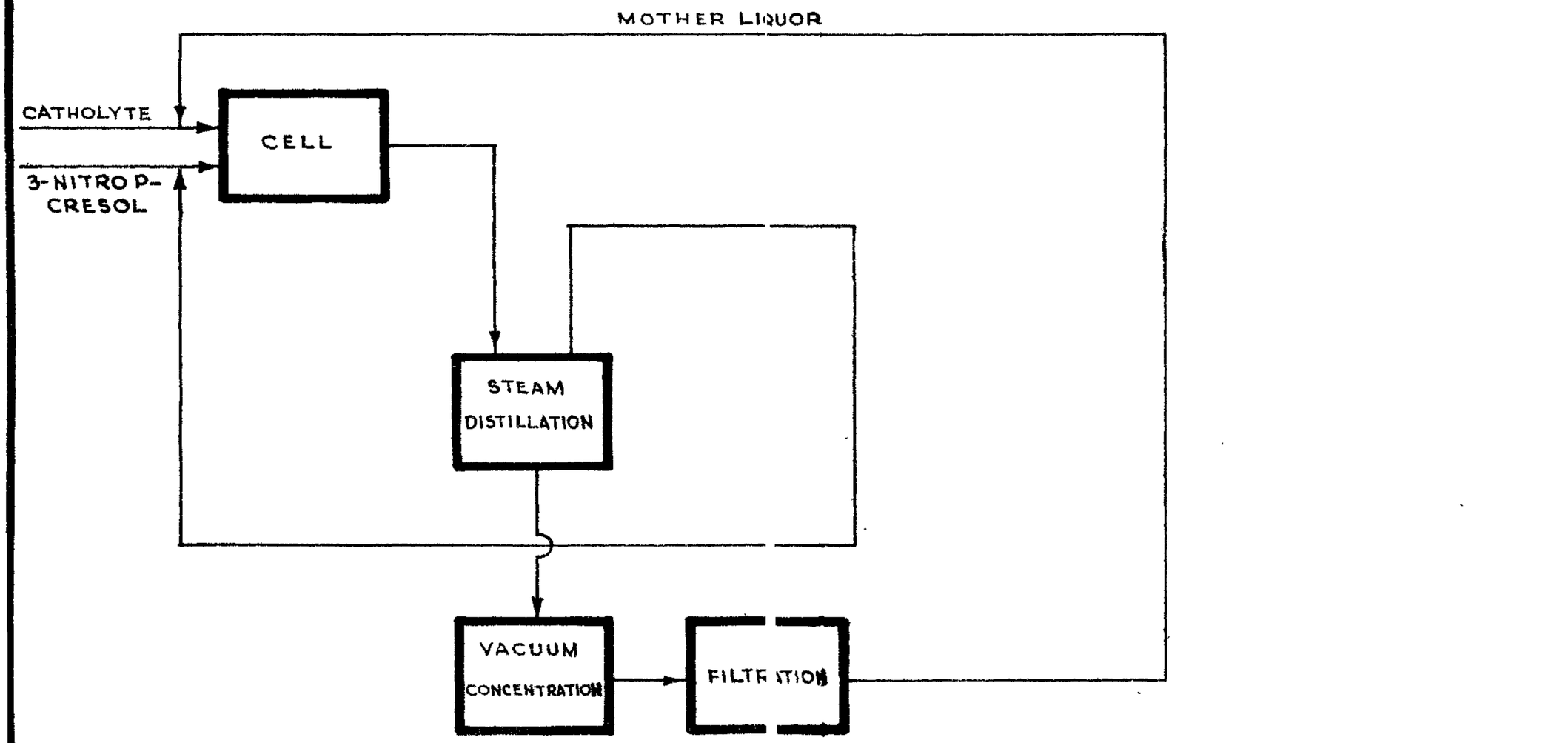

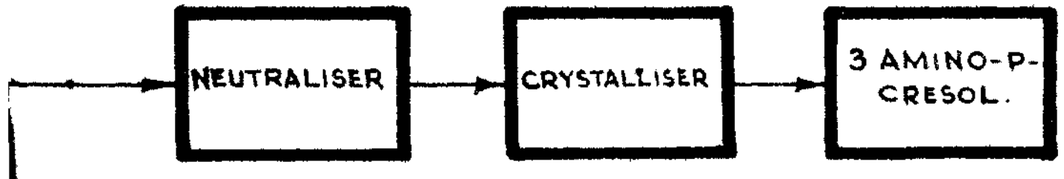

FIG. 2. BLOCK TYPE FLOW SHEET FOR THE PROCESS.

R B Pai
(R.B. PAI)
PATENTS OFFICER,
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