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A PROCESS FOR THE PRODUCTION OF BENZYL ALCOHOL.

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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, KALICHETTY NATARAJAN and KODETHOOR SHRIVARA UDUPA, all of the Central Electrochemical Research Institute, Karaikudi-3, India, all Indian citizens.

Benzyl alcohol is greatly valued for the esters it forms with the acetic, benzoic and sebasic acids and also to a lesser extent for those with formic, propionic, butyric, valeric, cinnamic and salicylic acids. The aliphatic esters are used principally by the soap, perfumery and flavour industries. Benzyl benzoate has considerable medical applications also (as does also the cinnamate) and is an effective insecticide for certain ticks and mites. Benzyl alcohol is also largely used in cosmetic, ink and lacquer industries. It readily dissolves casein and gelatin at elevated temperatures and is an important ingredient in the preparation of certain acid resistant cements and resins. Solutions of benzyl alcohol have found some use as local anesthetics. Pure alcohol has some antiseptic properties and in the form of an ointment or lotion it is effective in preventing or relieving itching.

Benzyl alcohol is normally prepared by the hydrolysis of benzyl chloride which yields a product that is not free from traces of chlorinated impurities. The alcohol so obtained requires very elaborate purification so that it may be used for the perfumery industry. A direct electrolytic reduction of benzoic acid to benzyl alcohol will give a product which will be completely free from traces of chlorinated products as there is no chlorinated intermediate involved in the production. There have not been any attempts in the past for the production of benzyl alcohol by such a reduction process and various investigations concerning the reduction of benzoic acid have been mostly confined to the laboratory. A systematic study on the reduction of benzoic acid to benzyl alcohol was made by Swann and co-workers in U.S.A. but they made the isolation more complicated by reducing an ethyl alcoholic solution of benzoic acid which made recovery of benzyl alcohol very difficult involving multi-component system for distillation. Loss of ethyl alcohol during electrolytic reduction makes the process economically not attractive on a large scale.

Studies carried out by us revealed that there is no need to add ethyl alcohol to the catholyte to favour solution of benzoic acid as was done by other workers. Such addition was also found to affect the rate of reduction. It was found out that direct reduction of benzoic acid as a suspension in sulphuric acid could be carried out very effectively by using a rotating cathode. Rotation of the cathode favours not only agitation of catholyte thereby ensuring saturation of same with benzoic acid but also the removal of benzyl alcohol. These enhance the rate of reduction permitting use of high current density.

The invented process for the production of benzyl alcohol consists in electrolytically reducing benzoic acid in suspension in dilute sulphuric acid (5 to 30%), using a rotating lead cathode at temperatures up to 90°C to 100°C, and current densities 1 to 50 amp|dm² wherein the oily product formed is isolated in stages, and wherein the cathode is washed to favour continuous reuse of the cathode as well as the dilute sulphuric acid (5 to 30%) used as catholyte.

Thus the reduction is carried out at a rotating lead cathode using sulphuric acid preferably 10% strength at temperatures ranging from 50-90°C but preferably at 85°C at a current density up to 30 to 40 amp|dm².

After separating the alcohol formed as an oily layer, the cathode is reused at least four times or more after washing it with water but without mechanical cleaning.

The sulphuric acid catholyte (preferably 10%) is used at least four times or more unless it becomes contaminated after separation of the oily product formed, in which case fresh electrolyte is employed.

The anolyte consists of 5 to 30 per cent sulphuric acid but preferably 30 per cent sulphuric acid.

An anode of perforated lead sheet is employed.

Thus, benzoic acid is electrolytically reduced to benzyl alcohol at elevated temperatures (80-90°C) using a rotating pure lead or pure lead covered or electroplated cathode (99·9 per cent) in a 10 per cent sulphuric acid bath at high current densities (30-40 amp|dm²). The current efficiencies are of the order of 80 per cent and above. Benzyl alcohol coming out as an oily layer can be easily separated thereby making the isolation a simple procedure. The cathode gets covered with a layer of alcohol which reduces the current efficiency considerably when the same cathode is reused in subsequent reductions. It is found that if the cathode is washed at this stage with water, the washing being done with the cathode rotating, the oily layer adhering on the cathode is effectively removed and the cathode can be used for further reductions of benzoic acid with the same electrolyte with good current efficiencies. The procedure of intermittent cleaning with water after removing the electrolyte restores the current efficiency which aspect had been overlooked by previous workers who noted that the cathode became ineffective in use. This feature of the investigation wherein the same cathode is effectively and repeatedly used without loss of current efficiency is something new.

The following procedure describes the manner of carrying out the process :

The cell (Fig. 1(a) of the accompanying drawings consists of a 3 litre Pyrex or Index beaker (A) cut to a height of 15 cm. A tight fitting lead cover (B) made out of pure lead (99·9%) sits tightly on the beaker by means of a groove in the cover. The lead cover carries holes for introducing a porous pot (5 cm dia. × 20 cm height) (P), cathode (C) (5 cm dia. × 15 cm), a thermometer (T) and a condenser (D). The cathode is made out of pure lead and attached to a copper shaft (S) (1·8 cm dia. × 20 cm) and rotated by a F. H. P. motor (not shown), the speed of which is adjusted through a variac (not shown). The anode (E) is a strip of lead (0·16 cm thick) roll into a cylinder (4 cm dia. × 20 cm) having perforations (0·6 cm dia). Fig. 1(b) is a plan of the cell assembly.

2 litres of 10 per cent sulphuric acid is used as catholyte (K) and 500 cc of 10 per cent sulphuric acid as anolyte (L). 50 g of technical grade benzoic acid (Z) is weighed into the catholyte (K) and the reduction is carried out at 30 amp|dm² and the temperature soon rises to 80-90°C when the benzoic acid dissolves. Further rise of temperature is avoided by cooling the cell externally (or internally) with cold water. The reduction proceeds smoothly and the escape of benzyl alcohol along with the vapour is prevented by maintaining a slight suction at the top of the condenser. After theoretical time (4F mole of benzoic acid) another lot of 50 g of benzoic acid is introduced into the bath and further reduction is carried out to the theoretical time. At this stage oil separates out and electrolyte along with the oil siphoned out and the oil separated with a separating funnel.

The cell is now filled with water (after cooling), and the cathode is rotated for half-an-hour when the adhering layer of alcohol on the cathode surface is removed. The electrolyte is then reintroduced into the cell and the reduction resumed with further quantities of benzoic acid (50 g) when again further separation of the oil occurs. The electrolyte is again syphoned out and the oil separated, and cathode cleaned as before. This makes the process continuous and the cathode reusable a number of times.

The benzyl alcohol separated from the electrolyte is washed with sodium carbonate solution to remove the unreduced dissolved benzoic acid and the benzyl alcohol is freed from aqueous layer and distilled under reduced pressure. The pressure shall be quite low so that the distillation takes place at as low a temperature as possible as otherwise the benzyl alcohol will polymerise resulting in a resinous product.

The following examples give the results obtained in typical experiments:

Example 1

Catholyte: 2 litres of 10 per cent sulphuric acid.
Anolyte: 500 ml of 10 per cent sulphuric acid.
Benzoic acid reduced: 50 g.
Cathode: Rotating lead.
Anode: Perforated lead.
Current density: 30 amp|dm².
Diaphragm: Ceramic porous pot.
Temperature: 85°C.
Duration of electrolysis: 54 minutes at 50 amp.

No oil separated out here and the electrolyte contained the alcohol formed.

Example 2

Conditions are same as in Example 1. A further quantity of 50 g of benzoic acid was added and electrolysed at 50 amp for 54 minutes. 30 cc of oil separated out after reduction. Current efficiency was 80% (calculated on the basis of product separated out). The cathode was washed with water at this stage and the electrolyte reintroduced.

Example 3

Conditions are same as before. A further quantity of 50 g of benzoic acid was added and electrolysed (54 minutes at 50 amp). Oil separated = 27 cc corresponding to a current efficiency of 75 per cent.

This procedure was repeated a number of times and in case the electrolyte is not to be reused, the benzyl alcohol could be completely recovered by neutralising the sulphuric acid with sodium carbonate and then salting out.

We claim:

1. A process for the production of benzyl alcohol which consists in electrolytically reducing benzoic acid in suspension in dilute sulphuric acid (5 to 30%), using a rotating lead cathode at temperatures upto 90°C to 100°C, current densities 1 to 50 amp|dm² wherein the oily product formed is isolated in stages, and wherein the cathode is washed to favour continuous reuse of the cathode as well as the dilute sulphuric acid (5 to 30%) used as catholyte.

2. A process as claimed in Claim 1 wherein the reduction is carried out at a rotating lead cathode using sulphuric acid of 10% concentration.

3. A process as claimed in Claims 1 and 2 above wherein the reduction is carried out at a current density up to 30 to 40 amp|dm².

4. A process as claimed in any of the above claims wherein the reduction is carried out at temperatures ranging from 50-90°C but preferably at 85°C.

5. A process as claimed in the above claims wherein after separating the alcohol formed as an oily layer, the cathode is reused at least four times or more after washing it with water but without mechanical cleaning.

6. A process as claimed in Claim 1 wherein the sulphuric acid catholyte (preferably 10%) is used at least four times or more unless it becomes contaminated after separation of the oily product formed, in which case fresh electrolyte is employed.

7. A process as claimed in any of the above claims wherein the anolyte consists of 5 to 30 per cent sulphuric acid but preferably 30 per cent sulphuric acid.

8. A process as claimed above wherein an anode of perforated lead sheet is employed.

9. A process for the production of benzyl alcohol by reduction of benzoic acid according to the process substantially as hereinbefore described.

R. BHASKAR PAI

Patents Officer,

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

Dated this 5th day of July 1963.

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ONE SHEET ONLY
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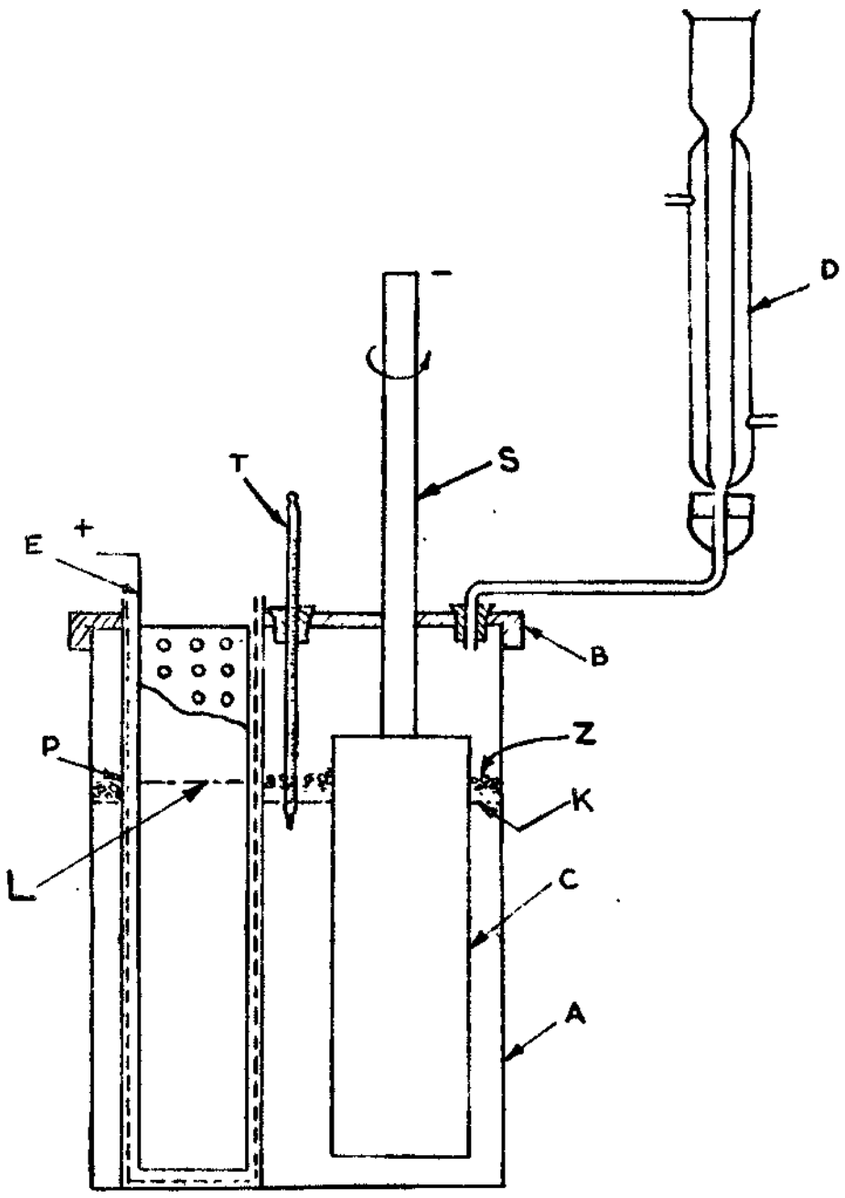

FIG. 1.(a)

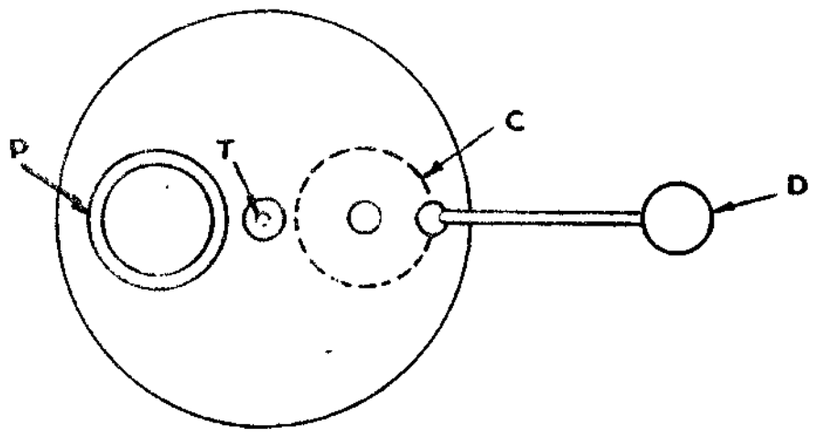

FIG. 1. (b)

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