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A PROCESS FOR THE ELECTROLYTIC PREPARATION OF SALICYLALDEHYDE.

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 VENKATKRISHNA UDUPA AND BIMAN BIHARI DEY, both of the Central Electro-Chemical Research Institute, Karaikudi, India, both Indian.

This invention relates to the electrolytic preparation of salicylaldehyde.

Electrolytic reduction of salicylic acid to salicylaldehyde was described by Hugo Weil in 1906 and two years later by Carl Mettler. Tesh and Lowy undertook an extensive study of this problem and suggested the use of sodium bisulphite to combine with the aldehyde formed and protect it from further reduction to alcohol. Using sodium sulphate as electrolyte in the presence of boric acid, they claimed a 55 per cent yield of salicylaldehyde. The results were disputed by a number of workers and recently May and Kobe re-investigated the problem and obtained a 50 per cent conversion, following their procedure. They also showed that the r.p.m. of the stirrer employed has a definite influence on the conversion of salicylic acid to salicylaldehyde.

As a result of the investigation carried out in the Central Electro-Chemical Research Institute the following observations have been made which are improvements over the prior procedures for obtaining salicylaldehyde. While realizing the need for boric acid in the catholyte, it has now been observed that there is a definite necessity for maintaining a critical pH range (5.4 to 6.4 and not exceeding 7) for the process.

The procedure adopted by Tesh and Lowy of using sodium sulphate (15g) and boric acid (15g) as electrolyte gives only about 28 per cent yield of salicylaldehyde when 10 per cent sodium sulphate solution is used as anolyte. It has however been observed by us that the yield can be increased to 55 per cent if only 10g of sodium sulphate and 30g boric acid are used in catholyte while using 10 per cent sodium sulphate solution as anolyte. The excess boric acid helps to maintain the critical pH range (5.4 to 6.4).

It has further been shown that it is necessary to add sodium salicylate solution in stages and not all of it in bulk, the sodium bisulphite being of course added in stages also. Further, when 14g of salicylic acid is reduced, it is found that only 12g of sodium bisulphite is sufficient and not 20g as was used by Tesh and Lowy.

It was also noted that 10 per cent sulphuric acid can replace sodium sulphate solution as anolyte in which case the boric acid content of catholyte can be reduced. The sulphuric acid of the anolyte helps to maintain the critical pH range.

Sodium chloride can replace sodium sulphate as electrolyte in which case chlorine is obtained as a by-product at the anode. Here again when 10 per cent sodium chloride solution is used as anolyte the boric acid content has to be more to maintain the acidity in the catholyte. When however 10 per cent hydrochloric acid is used as anolyte, the boric acid content of catholyte can be decreased.

There are decidedly certain advantages in replacing sodium sulphate by sodium chloride as electrolyte and in replacing neutral salt solutions by corresponding acids, as anolyte. When a current density of approximately 12 amps/dm² was employed the cell voltage was above 20 volts for the sodium sulphate catholyte—sodium sulphate anolyte system. It was nearly 14.5 volts for sodium sulphate catholyte—sulphuric acid anolyte system. In the case of sodium chloride anolyte—sodium chloride catholyte system the voltage was still less. The sodium chloride catholyte—hydrochloric acid system had the lowest cell-voltage making it commercially a more suitable and economical procedure to follow. Also in this last case the yield was always 55 per cent whereas in the other cases the yield fluctuated between 50 to 55 per cent.

Amalgamated copper cathode is reported to give only traces of aldehyde. 10 per cent yield of salicylaldehyde was obtained by using a stationary amalgamated copper cathode. When a rotating amalgamated copper or brass disc-type cathode (illustrated in Fig. 2, E of the accompanying drawings) was used 40 to 45 per cent yield of salicylaldehyde has been obtained.

It has been found further that sodium sulphite can replace sodium bisulphite for fixing the aldehyde. However the catholyte becomes alkaline during the course of electrolysis and only 29 per cent yield of aldehyde is obtained. If in the other hand acid is added during electrolysis to neutralize the alkali the critical pH range is maintained and the usual yield of salicylaldehyde is obtained.

EXAMPLE 1. (Fig. 1.)

10g sodium sulphate and 30 g boric acid are added into 120 cc water. A layer (A) of mercury (2 lbs.) at the bottom of a 600 cc beaker (B) served as cathode. 14 g of salicylic acid neutralised with equivalent volume of 3N sodium hydroxide was added in 5 cc lots every 5 minutes. A total of 12 g sodium bisulphite was added in one gram lot every 5 minutes, two grams added in the first five minutes period.

Contact with mercury was effected by means of a small platinum wire fused to one end of a glass tube (C). This tube is filled with mercury and the cathode terminal is inserted into the same. A small porous pot (D) resting on a glass tripod kept inside the beaker served as anode chamber. 10 per cent sodium sulphate solution was used as anolyte. A current of 6 amps. was passed (c.d. 12 amps/dm²) for the theoretical period of time (56 minutes). Temperature was maintained at 15°—18°C. Cell voltage was 20 to 22 volts and at times more.

Solution of Product.—Catholyte was stirred for half an hour after electrolysis and then separated from mercury. It was then neutralized with 20 cc of concentrated sulphuric acid diluted to 100 cc and steam-distilled in a one-litre flask. The oil from the distillate was ether extracted and the extract washed with sodium bicarbonate solution, dried over anhydrous sodium sulphate and the ether distilled off. Yield of salicylaldehyde varied from 53 to 55 per cent.

EXAMPLE 2.

15 g of sodium sulphate and 15 g boric acid in 120 cc water served as catholyte. Sodium salicylate solution and sodium bisulphite are added in stages at 5 minute intervals as before. 50 cc of 100 per cent sulphuric acid as anolyte with lead as anode. Temperature was 12°—16°C. 6 amp. current was passed for theoretical time (54 mins.). Cell voltage was 14 to 14.5 volts.

Yield of salicylaldehyde=53 per cent.

This example shows that 10 per cent sulphuric acid can replace 10 per cent sodium sulphate solution as anolyte in which case the boric acid content of catholyte can be reduced. The sulphuric acid of the anolyte helps to maintain the critical pH of catholyte. Cell voltage also is reduced by this.

EXAMPLE 3.

Use of Sodium Chloride as Electrolyte.

The following example illustrates the replacement of sodium sulphate by sodium chloride as electrolyte in which case chlorine is obtained as a by-product at the anode. Here again, it will be seen from the amounts specified below, that when 10 per cent sodium chloride solution is used as anolyte, boric acid content of catholyte has to be more to maintain the acidity.

10 g sodium chloride and 30 g boric acid in 120 cc water was catholyte. Salicylic acid (14 g) and sodium bisulphite (12 g) are added stagewise as before. Graphite anode was used and 10 per cent sodium chloride solution as anolyte. Chlorine was removed by suction. 6 amps. current was passed for theoretical time (54 mins.) at 15°—18°C. Yield of salicylaldehyde was 53-55 per cent.

EXAMPLE 4.

The following example illustrates the replacement by 10 per cent hydrochloric acid of 10 per cent solution of sodium chloride as anolyte while using sodium chloride as electrolyte in the reduction of salicylic acid.

15 g sodium chloride and 15 g boric acid in 120 cc water served as catholyte. 14 g salicylic acid neutralised with 3N alkali and 12 g sodium bisulphite were added stagewise. 50 cc of 10 per cent hydrochloric acid was anolyte and graphite was anode. Cell arrangement and working up of the product was carried out as in example 1. 6 amps. current was passed for theoretical time at 10°—14°C. Cell voltage was from 7.5 volts to 9.5 volts. Yield of salicylaldehyde was 55 per cent or more.

As will be seen, the cell voltage is very low because of this and the boric acid content can be reduced also. The cell can be readily maintained at a low temperature and the process becomes economical for practical scale production.

EXAMPLE 5 (Fig. 2).

Use of Rotating Amalgamated Cathode.

Amalgamated copper is reported to give only traces of aldehyde and on re-investigating a 10 per cent yield was obtained when the cathode was at rest. When a rotating amalgamated copper or brass disc-type cathode (Fig. 2, E) was used 40 to 45 per cent yield of salicylaldehyde was obtained following any of the above experimental conditions.

EXAMPLE 6.

Use of Sodium sulphite instead of Sodium Bisulphite for fixing the Aldehyde.

15 g sodium sulphate and 15 g boric acid in 120 cc water was the catholyte. 14g salicylic acid neutralized with 3N sodium hydroxide was added in 5cc lots every 5 minutes 9 g of sodium sulphite was added in 1.5 g lots every 5 minutes, 2 lots being added in the first five minute period. Later another 6 g sodium sulphite was added in one gram lot every 5 minutes. Thus 15g sodium sulphite was added in all. 2 cc of 6N sulphuric acid was added every 5 minutes during the course of electrolysis. 10 per cent sulphuric acid was used as anolyte. 6 amps current was passed for theoretical time at 14°—18°C.

Yield of salicylaldehyde was 55 per cent.

This example shows that sodium sulphite can equally replace sodium bisulphite for fixing the aldehyde. It is found that the tholyte soon becomes alkaline during the course of electrolysis and reduction of salicylic acid is stopped. The yield is only 29 per cent. If, on the other hand, sufficient acid is added during the electrolysis to neutralize the alkali and maintain the critical pH, then the usual yield is obtained.

EXAMPLE 7.

Using sodium chloride as electrolyte and 10 per cent hydrochloric acid as anolyte, 2 cc of 6N hydrochloric acid was added at intervals, all other conditions being same as above. 55 per cent salicylaldehyde has been obtained.

Price : TWO RUPEES.

We claim :

1. A process for the preparation of salicylaldehyde which consists in the electrolytic reduction of salicylic acid, using sodium sulphate as electrolyte in the presence of boric acid, and wherein a critical pH range, 5.4 to 6.4 and not exceeding 7, is maintained.
2. A process as claimed in Claim 1 wherein for reducing 14 g of salicylic acid, 10 g of sodium sulphate and 30 g boric acid are used in catholyte while using 10 per cent sodium sulphate solution as anolyte.
3. A process as claimed in Claim 2 wherein sodium bisulphite is added to fix the aldehyde formed.
4. A process as claimed in any of the preceding claims wherein 10 per cent sulphuric acid is used instead of sodium sulphate solution as anolyte and the boric acid content of the catholyte is reduced to maintain the aforesaid critical pH range.
5. A process as claimed in Claim 1 wherein sodium chloride is used instead of sodium sulphate as electrolyte, resulting in chlorine as a by-product at the anode.
6. A process as claimed in Claim 5 wherein 10 per cent hydrochloric acid is used as anolyte and the boric acid content of catholyte is decreased to maintain the aforesaid critical pH range.
7. A process as claimed in any of the preceding claims wherein a current density of approximately 12 amps/dm² is employed.
8. A process as claimed in any of the preceding claims wherein a stationary amalgamated copper cathode is employed.
9. A process as claimed in any of the preceding Claims 1 to 8 wherein a rotating amalgamated copper or brass disc-type cathode is used.
10. A process as claimed in Claim 3 wherein sodium sulphite is used instead of sodium bisulphite.
11. A process as claimed in Claim 10 wherein acid is added during electrolysis to neutralize the alkali and maintain the aforesaid critical pH range.

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Council of Scientific & Industrial Research.

Dated this 25th day of August 1954.

COUNCIL OF SCIENTIFIC &
INDUSTRIAL RESEARCH
NO. 52631.

TWO SHEETS
SHEET 1.

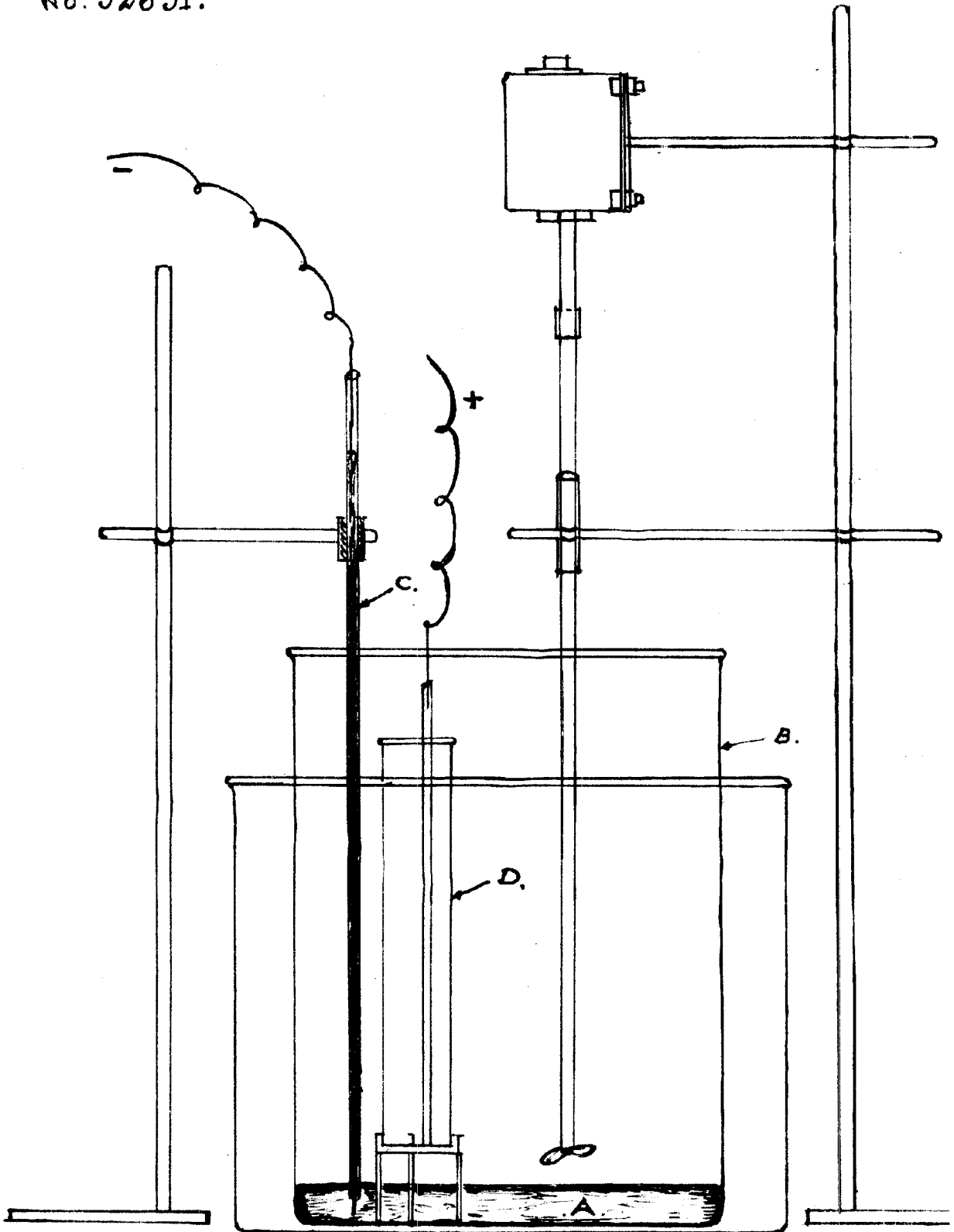


FIG. 1.

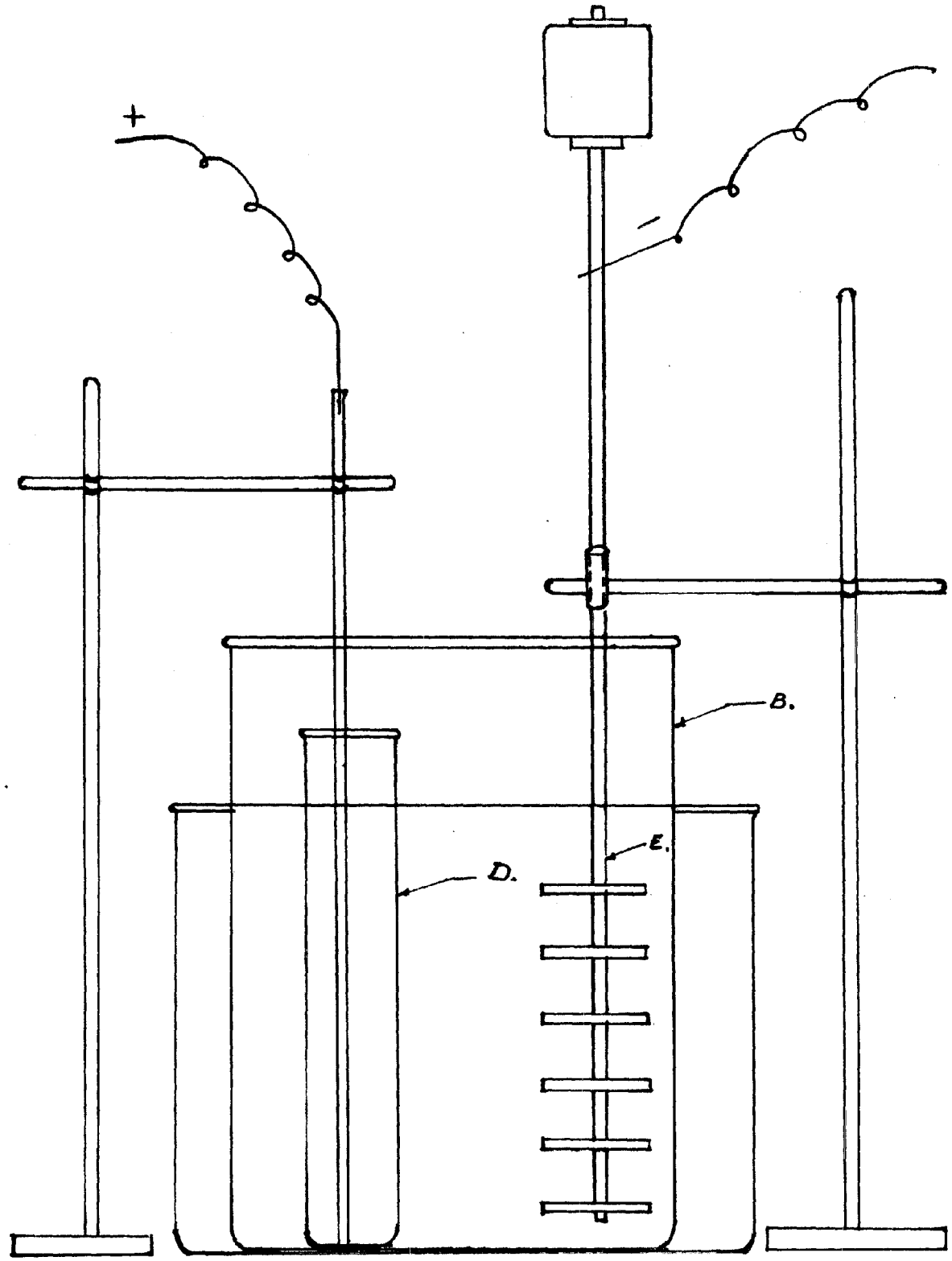


FIG. 2

.FIG. 2.

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