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"Improvements in or relating to electrochemical oxidation of ortho toluene sulphonamide to saccharin".

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, Rafi Marg, 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 (1) HANDADY VENKATAKRISHNAN UDUPA, Scientist, (2) MYSORE SESHAIYER VENKATACHALAPATHY, Scientist and (3) SANKARA NARAYANAIYER CHIDAMBARAM, Scientist all of the Central Electrochemical Research Institute, Karaikudi 6, India, all Indian citizens.

PRICE: TWO RUPEES

The main object of the invention is to obviate the draw backs mentioned earlier by the modifications and improvements now effected by us.

We have found that expensive oxidising agents like potassium permanganate and potassium dichromate are avoided by the process of electrolytic oxidation of chromic sulphate to chromic acid, oxidation of ortho toluene sulphonamide to saccharin, followed by the reoxidation of chromic sulphate to chromic acid in a cyclic manner.

The present process is superior to the processes hitherto described in literature since it does not involve the use of expensive oxidising agents, which increased the final cost of the product. The product isolation is simplified and the type of unit operations involved in the invented two stage process are such that it would very much help in the scale up of the process for the large scale adoption.

Our prior Indian Patent No. 95425 relates to a process for the regeneration of chromic acid for the oxidation of organic compounds in particular to p-nitrotoluene wherein the electrolytic regeneration of chromic acid from chromium sulphate and sulphuric acid is carried out using a lead dioxide anode either stationary or rotating and a lead cathode, closely wrapped with asbestos fibre.

According to the present invention, there is provided a cyclic process for the preparation of saccharin by electrochemical oxidation of ortho toluene sulphonamide with chromic acid and sulphuric acid characterised in that chromic acid obtained by the process as claimed in Indian Patent No. 95425 is used, the chromium sulphate obtained in the reaction mass by above stated electrochemical oxidation of o-toluene sulphonamide is purified to remove organic matter and is sent to regenerate chromic acid by the process of said patent No. 95425 and the chromic acid thus obtained is again used with sulphuric acid to oxidise o-toluene sulphonamide to saccharin in a cyclic process.

The regeneration of chromic acid may be carried out as follows: a) A current density of 2.5 - 5.0 A/dm^2 is employed while using a stationary anode and a current density in the range of 15-20 A/dm^2 is employed while using a rotating anode; (b) Temperature of electrolysis is kept at 40-45°C (c) Lead or lead alloy is used as anode material (d) Copper rod, covered with lead on which blue asbestos thread is closely wrapped, is used as cathode (e) The concentration of sulphuric acid is kept at 30-35% in the electrolyte and (f) The concentration of chromium sulphate is kept at 25-30% in the electrolyte.

Thus the oxidation of chromic sulphate to chromic acid and oxidation of ortho toluene sulphonamide to saccharin is followed by purification for removal of organic matter and reoxidation of chromium sulphate.

The oxidation may be carried out by taking electrolytically regenerated chromic acid in a reactor fitted with an efficient agitator, adding o-toluene sulphonamide to chromic acid, and gradually regulating the course of the reaction by the control of temperature.

Thus the oxidation of o-toluene sulphonamide (I) is carried out at a temperature of 55-60°C using electrolytically regenerated chromic acid in 50-55% aqueous sulphuric acid by the stagewise addition of (I) in equal quantities during the course of an hour.

Chromic acid obtained from the electrolytic cell may be allowed to react with ortho toluene sulphonamide in a separate reactor. The oxidation is carried out at 35 to 70°C but preferably at 60°C.

The process for the preparation of saccharin makes cyclic on a practical scale oxidation of chromic sulphate to chromic acid, oxidation of ortho toluene sulphonamide to saccharin and purification for removal of organic matter followed by reoxidation of chromium sulphate.

Thus, the first stage consists in the oxidation of chromic sulphate to chromic acid in an electrolytic cell; the second stage consists in the oxidation of ortho toluene sulphonamide to saccharin and the chromium sulphate thus obtained after purification is sent back to the cell for the regeneration of chromic acid to make the process cyclic.

Thus, the oxidation is carried out by taking electrolytically regenerated chromic acid in a reactor fitted with an efficient agitator, o-toluene sulphonamide is added to chromic acid, gradually regulating the course of the reaction by the control of temperature.

The conditions under which good yield can be obtained are as follows:

i) Temperature of oxidation at about 55-60°C

ii) The percentage of chromic acid is kept between 12 and 14%

iii) The percentage of sulphuric acid is is kept between 50 and 55%

O-toluene sulphonamide is added in stages by the addition of equal quantities during the course of an hour.

Typical examples:

EXAMPLE I

60 g of chromic acid was taken in 500 cc of 50% sulphuric acid. 46 g of ortho toluene sulphonamide was added and the reaction was carried out at a temperature range of 35-70°C. After the reaction was over, it was cooled to 10°C and filtered. The filtrate was electrolysed and 54 g of chromic acid was regenerated with a current efficiency of 50% for an yield of 90%. ~~22x2%~~ 29.1 g of saccharin was obtained with an yield of ~~22~~ 75% on the basis of o-toluene sulphonamide consumed during the reaction (36.2 g). M.P. of saccharin - 227°C. Energy consumption- 16-17 kwh/kg of saccharin.

EXAMPLE II

360 g of regenerated chromic acid in 3 litres of 50% sulphuric acid was taken in a reaction vessel and 200 g of ortho toluene sulphonamide was added. The reaction was carried out in the temperature range of 35-70°C. The product was isolated as mentioned in the previous example. 120 g of saccharin was obtained with an yield of 75% on the basis of ortho toluene sulphonamide consumed (150 g). The filtrate was electrolysed to regenerate chromic acid. A current efficiency of 52% with an yield of 88% was obtained. M.P. of saccharin- 227°C. Energy consumption - 16 to 17 kwh/kg of saccharin

EXAMPLE III

Chromium sulphate (890 g in 3.5 litres) obtained after the oxidation of o-toluene sulphonamide was electrolysed for the regeneration of chromic acid in an electrolytic cell. A stationary lead anode was used and the current density employed was 2.5 A/dm^2. A copper rod

covered with lead on which blue asbestos thread was closely wrapped, was used as cathode. The concentration of sulphuric acid in the electrolyte was 30%. During the electrolysis, the temperature of the cell was kept at about 40-45°C. After passing 362 a hrs, 382 g of chromic acid with an yield of 84.8% and a current efficiency of 76.4% was obtained.

Thus the invented process for the electrolytic production of saccharin from ortho toluene sulphonamide eliminates the use of expensive oxidising agents like potassium permanganate and potassium dichromate which increases the final cost of the product. The oxidation of ortho toluene sulphonamide by chromic acid, in a two stage processes, renders it suitable for large scale adoption.

We Claim

1) A cyclic process for the preperation of saccharin by electrochemical oxidation of ortho toluene sulphonamide with chromic acid and sulphuric acid characerised in that chromic acid obtained by the process as claimed in Indian Patent No. 95425 is used, the chromium sulphate obtained in the reaction mass by above stated electrochemical oxidation of o-toluene sulphonamide is purified to remove organic matter and is sent to regenerate chromic acid by the process of said patent No. 95425 and the chromic acid thus obtained is again used with sulphuric acid to oxidise o-toluene sulphonamide to saccharin in a cyclic process.

2) A process as claimed in claim 1 wherein the regeneration of chromic acid is carried out as follows:

a) a current density: 2.5 - 5.0 A/dm^2 is employed while using a stationery anode and a current density in the range of 15-20 A/dm^2 is employed while using a rotating anode;

b) temperature of electrolysis is kept at 40-45°C;

c) Lead or lead alloy is used as anode material;

d) copper rod, covered with lead on which blue asbestos thread is closely wrapped, is used as cathode;

e) the concentration of sulphuric acid is kept at 30-35% in the electrolyte and;

f) the concentration of chromium sulphate is kept at 25-30% in the electrolyte.

3) A process as claimed in claim 1 or 2 wherein the oxidation of chromic sulphate to chromic acid and oxidation of ortho toluene sulphonamide to saccharin is followed by purification for removal of organic matter and reoxidation of chromium sulphate.

4) A process as claimed in any of the preceding claims wherein the oxidation is carried out by taking electrolytically regenerated chromic acid in a reactor fitted with an efficient agitator, o-toluene sulphonamide is added to chromic acid, gradually regulating the course of the reaction by the control of temperature.

5) A process as claimed in any of the preceding claims wherein the oxidation of o-toluene sulphonamide (I) is carried out at a temperature of 55-60°C using 12-14% electrolytically regenerated chromic acid in 50-55% aqueous sulphuric acid by the stagewise addition of (I) in equal quantities during the course of an hour.

6) A process as claimed in any of the preceding claims wherein chromic acid obtained from the electrolytic cell is allowed to react with ortho toluene sulphonamide in a separate reactor.

7) A process as claimed in claim 6 wherein the oxidation is carried out at 35 to 70°C but preferably at 60°C.

8) A process for the preparation of saccharin substantially as herein before described.

Dated this 14th day of January 1976

R B Shashare Rai

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