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A PROCESS FOR THE OXIDATION OF TOLUENE TO BENZALDEHYDE.

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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, MYSORE SHESHAIYER VENKATACHALAPATHI AND RENGANATHAN RAMASWAMY, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, INDIA, ALL INDIAN CITIZENS.

The first successful attempt at the electrolytic oxidation of toluene to benzaldehyde was perhaps that of Perkin and Law who obtained a 7-8 per cent. yield of the aldehyde, although still earlier references to the process are found in the literature. Next in importance was the fairly exhaustive investigation carried out by Mitchell, who studied the use of inorganic carriers for oxidation of toluene. He used manganese sulphate (4 per cent.) in 55 per cent. sulphuric acid and reported 61 per cent. current efficiency for benzaldehyde formation if the toluene was removed quickly and the product recovered. A recent Japanese paper reports nearly 79-80 per cent. current efficiency, using the technique of superimposing A.C. on D.C. None of these processes have been adopted to practical scale operation with continued maintenance of such high efficiencies. Other attempts at working out a practical scale process for the electrolytic production of benzaldehyde have also not proved successful so far.

All the above workers used stationary anodes in their process. An attempt at the use of rotating anode was first made by Dey and Maller who reported no improvement in the yield. Experiments have now been done to carry out the preparation on the lines suggested by Mitchel and by the Japanese authors. In both cases the current efficiency remained fairly high in the initial stages of electrolysis but later decreased considerably, so that even by continuous circulation of toluene the overall current efficiency could not be increased to more than 14 per cent. Rotation of the anode also did not help in increasing the current efficiency of the process.

The invented process for the preparation of benzaldehyde consists in oxidising toluene with manganic sulphate obtained by electrolytic oxidation of a paste of manganous sulphate in sulphuric acid as described in co-pending patent application No. 62379.

The process developed now consists in taking a suspension of manganous sulphate in 53 per cent. sulphuric acid and oxidising it to manganic sulphate electrolytically as described in an earlier patent and using the paste of manganic sulphate so obtained in a separate reactor to oxidise toluene to benzaldehyde. The manganous sulphate formed in the electrolyte has to be given a vacuum treatment until a few ml. of the distillate has collected; this step removes all the volatile organic matter and the remaining electrolyte after making up to the required strength is reoxidised to manganic sulphate in the electrolytic cell and used once again for oxidation of a further quantity of toluene as before. In this way, the process is made continuous and cyclic, the manganous sulphate and the sulphuric acid being used for a number of experiments. The toluene is oxidised by manganic sulphate at 50 to 100° C. but preferably at 55° C. in a separate reactor in order to yield benzaldehyde with an overall current efficiency of 40 to 50 per cent. After separating the toluene layer from the paste benzaldehyde is recovered from toluene layer either by fractional distillation or by fixing the aldehyde as a bisulphite addition compound which is later decomposed and steam-distilled. The process is described in detail in the following paragraphs.

Oxidation of toluene to benzaldehyde:

Toluene is treated with the paste of manganic sulphate obtained by the process described in the co-pending patent application No. 62379 in an agitator provided with a reflux condenser to prevent loss of toluene. Oxidation could be carried out at 40° to 100° C. the duration of oxidation being reduced by increasing the temperature. But at higher temperatures, considerable resinification takes place leading to lower yields. It is immaterial whether the toluene is added in one lot or in stages, a slight advantage in the latter being offset by the number of stages and the labour involved. 1 to 10 ml. or more of toluene for every gram of manganese sulphate employed in the paste will have to be used but about 2 cc. would give the required result. It is immaterial how much is used if the aldehyde is isolated as the bisulphite addition compound, but if the toluene and benzaldehyde are recovered by distillation it is economical to use the optimum amount of toluene mentioned above. The temperature of oxidation could be about 60° C. The paste of manganic sulphate and toluene are agitated until the pink colour of the acid disappears on completion of oxidation.

Isolation of benzaldehyde and other products:

The toluene layer is separated from the paste and if necessary the paste is again extracted with a small amount of fresh toluene and the toluene extracts all collected together. A wash with soda ash solution removes any benzoic acid and also serves to remove any sulphuric acid. The aqueous portion on acidification would give any benzoic acid formed in the reaction. The toluene is then fractionally removed leaving behind benzaldehyde and other products, if any, like benzyl alcohol, dibenzyl ether, benzyl benzoate and any resinous matter. The benzaldehyde is recovered by distillation.

An alternate procedure would be to treat the toluene layer after removal of benzoic acid, with a saturated solution of sodium bisulphite so that the bisulphite addition compound of benzaldehyde separates out which can be filtered off, dried and then steam-distilled after either neutralisation with soda ash or sulphuric acid. In the latter case the sulphur dioxide evolved could be reabsorbed to give further bisulphite. The aldehyde obtained as steam-distillate is separated and then distilled again to give benzaldehyde in the purest form.

The paste after separation of the toluene layer followed by an extraction with toluene is recycled to the electrolytic cell for regeneration of manganic sulphate as described in co-pending application No. 62379. The overall current efficiency for oxidation of toluene to benzaldehyde varies from 38 to 48 per cent., taking all different cycles of the operation. The energy consumption per lb. of benzaldehyde works out to 3.54 Kw-hr. (D.C.) assuming 43 per cent. overall current efficiency.

EXAMPLES.

200 gms. of manganous sulphate in 700 cc. of 55 per cent. sulphuric acid was oxidized by passing 44 amp.-hrs. at 5 rmp./dm.^{2} at 50-55° C. using a rotating lead anode (1" diam. and anode area immersed being 1.2 dm.^{2}). The cell voltage was 2.9 to 3 volts. The current efficiency at the anode was 84.9 per cent.

400 cc. of the toluene was added at 55° C. and the benzaldehyde formed was isolated by the bisulphite treatment as described above. Weight of benzaldehyde obtained was 22 gms. The current efficiency came to 49.5 per cent. The experiment was continued with the same electrolyte and in the second and third experiments 21.6 and 18 g. respectively were obtained giving 48.5 per cent. and 40.5 per cent. current efficiency. In a second series of experiments, 22, 18 and 17.6 gms. of benzaldehyde were obtained, the current efficiencies being 49.5 per cent., 40.5 per cent. and 40 per cent. respectively.

In another series of experiments carried out similarly as above, benzaldehyde was isolated by fractional

distillation as described earlier. A total of 64.6 gms. of benzaldehyde was obtained in four experiments giving an average current efficiency of 40 per cent.

We claim:

1. A process for the preparation of benzaldehyde which consists in oxidising toluene with manganic sulphate obtained by electrolytic oxidation of a paste of manganous sulphate in sulphuric acid as described in co-pending patent application No. 62379.

2. A process as claimed in Claim 1 wherein the paste of manganic sulphate obtained from the electrolytic cell is allowed to react with toluene by agitation in a separate reactor.

3. A process as claimed in Claim 2 wherein the oxidation is carried out at 40° to 100° C., but preferably at 60° C.

4. A process as claimed above wherein more than the theoretical quantity of toluene is taken for oxidation, based on the manganous sulphate started with.

5. A process claimed in any of the claims above wherein the benzaldehyde is recovered from excess toluene either by steam distillation, fractional distillation or as bisulphite addition compound which is decomposed and the aldehyde recovered by steam-distillation.

6. A process as claimed in any of the previous claims wherein the processes of oxidation of manganous sulphate to manganic sulphate, oxidation of toluene to benzaldehyde and vacuum treatment for removal of volatile organic matter followed by reoxidation of manganeous sulphate are made cyclic and continuous on a practical scale.

7. Benzaldehyde prepared by oxidation of toluene by manganic sulphate according to the process as herein before described.

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