PROVISIONAL SPECIFICATION

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OLD MILL ROAD, NEW DELHI, INDIA, AN INDIA INDIAN REGISTRATION FUND INCORPORATED UNDER THE REGISTRATION OF SOCIETIES ACT (ACT XXI OF 1860).

THE FOLLOWING SPECIFICATION DESCRIBES THE NATURE OF THIS INVENTION.

Invention No. S 523a

The first successful attempt of the electrolytic oxidation of xylenes to the corresponding aldehydes was perhaps that of Law and Perkin who obtained an yield of 10-20% by passing current for nearly double the time that is theoretically required. The reaction was carried out in a separate reactor to the corresponding aldehydes. The xylene aldehyde was then obtained by the reaction of the xylene with a suitable reagent to yield p-tolualdehyde with an overall current efficiency of 45-50%. The xylene was oxidized at 20-40°C but preferably at 35-35°C and m-xylene was oxidized at 35-50°C but preferably at 40°C. In the case of mixed xylenes the temperatures is kept between 35-35°C. After the reaction is over the xylenes remains are separated from the electrolyte and the aldehyde is isolated either by fractional distillation or by freezing it as a bismuthate addition compound. It was then stored at liquid nitrogen and was used for a number of experiments.

Xylanedi oxide was mixed with m-xylene and a solution was added to the mixture. The mixture was oxidized with a current of 10 amperes at 40°C. The current efficiency was found to be 40% and the xylene was recovered.

Examples

1. Preparation of p-Tolualdehyde:

The procedure is the same as described above except that the xylene is used instead of p-xylene. The current efficiency was found to be 45% and the xylene was recovered.

2. Preparation of m-Tolualdehyde:

The procedure is the same as described above except that the xylene is used instead of m-xylene. The current efficiency was found to be 45% and the xylene was recovered.

Price: Two Rupees.
3. Oxidation of p-Xylene in m-Toluiddehyde:

The procedure is quite analogous to p-xylene as described earlier and m-xylene is employed instead of p-xylene. Oxida-
tion could be carried out at 35-50°C but preferably at 40°C.

Isolation of m-Toluiddehyde and other products

The method employed is quite similar to p-toluiddehyde and the overall current efficiency varies from 25 to 40%, taking all different cycles of operation. The energy consumption per lb. of m-toluiddehyde works out to 4.1 kw-hr (D.C.) assuming 40% overall current efficiency.

Examples

Manganous sulphate was prepared as described earlier. 400 cc of m-xylene was added at 40°C and the m-toluid-
hyde was isolated by the sodium bisulphite treatment as described earlier. Weight of m-toluiddehyde obtained was 16 gms giving a current efficiency of 40%. The experiments were continued with the same electrolyte and in the second and third experiments 16 and 18.2 g respectively were obtained giving 40% and 36% current efficiency. In a second series of experiments, 16, 15 and 30 g of m-toluiddehyde were obtained, the current efficiency being 40%, 40% and 37.5% respectively.

4. Oxidation of Mixed Xylenes and Mixed Aldehydes:

The method is similar to the oxidation of p-xylene as described earlier. The mixed xylenes supplied by Central Scientific supplies was used and it contained meta and ortho xylene. Oxidation could be carried out at 35-50°C but preferably at 40°C.

Isolation of the Aldehydes

The method employed is quite similar to m-toluiddehyde and the overall current efficiency varies from 25 to 40%, taking all different cycles of operation. The energy consumption per lb. of the mixed aldehydes works out to 4.1 kw-hr (D.C.) assuming 40% overall current efficiency.

Examples

Manganous sulphate was prepared as described earlier under p-xylene oxidation. 400 cc of the mixed xylenes was added at 40°C and the mixed aldehydes were isolated by sodium bisulphite method as described earlier. Weight of mixed aldehydes was 16 gms giving a current efficiency of 40%. Subsequent runs with the same electrolyte gave a current efficiency of 60% and 30% respectively.

The following are among the noteworthy features of this invention:

(1) A process for the preparation of m-toluiddehyde (2) m-toluiddehyde (iii) m-toluiddehyde (iv) mixed toluiddehydes, which consists in oxidizing the corresponding xylenes with manganous sulphate obtained by electrolytic oxidation of a paste of manganous sulphate in sulphuric acid as described in Patent No. 62135.

(2) A process as in (1) wherein the paste of manganous sulphate obtained from the electrolytic cell is allowed to se-
sect with ortho, meta, para xylenes and mixed xylenes by agitation in a separate reactor.

(3) A process as in (2) wherein the oxidation of p-xylene, o-xylene, m-xylene and mixed xylenes is carried out at 25°, 30°, 40° and 45°C respectively.

(4) A process as above wherein 0.5 to 5 cc or more of the respective xylene is taken for oxidation for every gram of manganous sulphate started with but preferably about 1 cc per gram.

(5) A process as above wherein the corresponding aldehyde formed is recovered from the anode corresponding xylenes either by fractional distillation or an alkaline addition compound which is decomposed to isolate the aldehyde or by the steam distillation of the whole emission.

(6) A process as above wherein the process of oxidation of m-xylene to m-nitroquinone, oxidation of o-xylene, and p-xylenes and mixed xylenes to o-toluiddehyde, m-toluiddehyde, p-toluiddehyde and mixed toluiddehydes and vacuum treatment of remnant for removal of volatile organic matter followed by recrystallization are made cycle on a practical scale.

(7) m-Toluiddehyde is prepared by oxidation of p-xylene by manganous sulphate according to the process as hereinbefore described.

(8) o-Toluiddehyde is prepared by oxidation of o-xylene by manganous sulphate according to the process as hereinbefore described.

(9) m-Toluiddehyde is prepared by oxidation of m-xylene by manganous sulphate according to the process as hereinbefore described.

(10) Mixed toluiddehydes are prepared by oxidation of mixed xylenes by manganous sulphate according to the process as hereinbefore described.

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Dated 1st day of December 1953.

COMPLETE SPECIFICATION.

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The following specification particularly describes and mentions the nature of the invention and the manner in which it is to be performed.

THIS IS AN INVENTION BY RAMDAS VENKATAKRISHNNA UPPA AND MYDROSBENAIYER VENKATACHALAPATHI OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KOLKATA, MADRAS, INDIA, BOTH INDIAN CITIZENS.

The first successful attempt of the electrolytic oxidation of xylenes to the corresponding aldehydes was perhaps that of Low and Parson, who obtained an yield of 10-15% by passing current for nearly double the time that is theoretically required.

It was also studied by Fletcher and Stokker but details were not given. None of the processes have been adopted to practical scale operation with maintenance of high current efficiency.

The process developed now consists in taking a suspension of manganous sulphate in 35% sulphuric acid and oxidizing it to manganous sulphate electrocally as described in Patent No. 20925. The paste thus obtained is used to oxidize the respective xylenes in a separate reactor to the corresponding aldehydes. The manganous sulphate formed after the reaction is given a vacuum treatment. This step removes all the volatile organic matter and the remaining electrolyte after taking up the required strength in acid is reoxidized to manganous sulphate in the cell and used once again for oxidation of a further quantity of xylenes as before. Thus the process is made continuous and cycle, the manganous sulphate and sulphuric acid being used for a number of experiments.

p-Xylene is oxidized by manganous sulphate at 25 to 40°C but preferably at 30°C in a separate reactor in order to yield p-toluiddehyde with an overall current efficiency of 40 to 50%. o-Xylene is oxidized at 25-40°C but preferably at 35°C and m-xylene is oxidized at 25-35°C but preferably at 40°C. In the case of mixed xylenes the temperature is kept between 35-
40°C. After the reaction is over the xylene layer is separated from the electrolyte and the aldehyde is isolated either by fractional distillation or by fixing it as a bisulphite addition compound which is later decomposed by soda ash and steam distilled. The processes are described in detail in the following paragraphs.

1. Oxidation of p-Xylene to p-Toluiddehyde:

p-Xylene is treated with the paste of manganous sulphate obtained by the process described in the Patent No. 20925 in an agitator provided with a reflux condenser to prevent loss of p-xylene. Oxidation could be carried out at 25 to 40°C the duration of oxidation being reduced by increasing the temperature. But at higher temperatures, considerable reduc-
isolation takes place leading to lower yields and the products are rather coloured. It is immaterial whether the p-xylene is added in the form of pure oil or as an aqueous solution in a slight excess in the latter being offset by the number of stages and the labor involved. 1 to 0.5 or more p-xylene for every gram of manganese sulphate employed in the paste will have to be used but about 5% would cover the required needs. It is immaterial how much is used if the aldehyde is isolated as the bisulphite addition compound but if the p-xylene and m-tolualdehyde are recovered by distillation it is economical to use the optimum amount of p-xylene mentioned above. The temperature of oxidation could be about 25°C. The reaction is carried out until the pink color of the acid disappears.

Isolation of p-Tolualdehyde and other products

The p-xylene layer is separated from the paste and if necessary the paste is again extracted with a small amount of p-xylene and the xylene extracts all solubled together. A wash with soda ash solution removes any pure acid and also serves to remove the mineral acid. The p-xylene is then fractionally removed leaving behind p-tolualdehyde and other products, if any, like xylol, xylolcarbinol, xylene and any resins etc. The p-tolualdehyde is recovered by distillation.

Another procedure would be to steam-distil the whole emulsion, especially when a minimum quantity of p-xylene is used, and the distillate is extracted with a saturated solution of sodium bisulphite and subsequently the addition compound of aldehyde is decomposed by sodium sulphite or sulphonic acid and then distilled. In the latter case the aldehyde dioxide liberated could be collected to give further bisulphites. The aldehyde obtained in the steam-distillation is purified, dried with anhydrous calcium chloride and distilled under vacuum to recover p-tolualdehyde in the pure form.

The reaction procedure would be to tease the p-xylene layer, after removal of p-xylene, with a saturated solution of sodium bisulphite and the addition compound of aldehyde is decomposed and distilled as before. The paste after separation of the p-xylene layer is filtered by (if necessary) an extraction with p-xylene is recycled to the electrolytic cell for regeneration of manganese sulphate as described in Patent No. 66728. The overall current efficiency for oxidation of p-xylene to p-tolualdehyde varies from 37 to 49%, taking all different cycles of the operation. The energy consumption per lb. of p-tolualdehyde works out to 4 kw-hr (C.C.) assuming 42% overall current efficiency.

Examples

200 gms manganese sulphate was dissolved in 200 c.c. of water and 200 c.c. of concentrated sulphuric acid was added with efficient stirring. The suspension was oxidized by passing 50 amp. hrs at 5 volts at 55-58°C using a rotating anode, 1 1/2 inches, and anode area increased by 1.5 sq. cm. The cell voltage was 3.5 to 3.8 volts. The current efficiency was 80%.

300 c.c. of p-xylene was added at 45°C and the p-tolualdehyde formed was isolated by the bisulphite treatment as described above. The current efficiency was 50%. Weight of p-tolualdehyde obtained was 20 gms. The experiment was continued to pass the same electrolyte for the second and third runs 10.5 and 16.5 g. respectively giving 45.4 and 41.5% current efficiency. In a second series of experiments, 25, 16 and 16 g of p-tolualdehyde were obtained, the current efficiencies being 91%, 45% and 40% respectively.

In another series of experiments carried out similarly as above, p-tolualdehyde was isolated by steam distillation of the emulsion as described earlier. A total of 78 gms of p-tolualdehyde was obtained in four experiments giving an average current efficiency of 46%.

2. Oxidation of o-Xylene to p-Tolualdehyde:

The procedure is the same as described in p-xylene and o-xylene is employed instead of p-xylene. Oxidation could be carried out between 25 to 40°C but preferably at 30°C.

Isolation of o-Tolualdehyde and other products

The methods are quite similar to the isolation of p-tolualdehyde as described earlier. The overall current efficiency for the oxidation to o-tolualdehyde varies from 70 to 85%, taking all different cycles of operation. The energy consumption per lb. of o-tolualdehyde works out to 4.1 kw-hr (C.C.) assuming 40% overall current efficiency.

Examples

Manganese sulphate was prepared as described earlier. 600 c.c. of m-xylene was added at 25°C and the o-tolualdehyde was isolated by the sodium bisulphite treatment as described earlier. Weight of o-tolualdehyde obtained was 15 gms. The current efficiency came to 45%. The experiment was continued with the same electrolyte and in the next experiments 15 and 25 g respectively were obtained giving 45% and 47.5% current efficiency. In a second series of experiments, 15, 18 and 25 g of o-tolualdehyde were obtained, the current efficiencies being 45%, 40% and 30.5% respectively.

3. Oxidation of m-Xylene to p-Tolualdehyde:

The procedure is quite analogous to p-xylene as described earlier and p-xylene is employed instead of m-xylene. Oxidation could be carried out at 35-50°C but preferably at 40°C.

Isolation of m-Tolualdehyde and other products

The method employed is quite similar to p-tolualdehyde and the overall current efficiency varies from 35 to 45%, taking all different cycles of operation. The energy consumption per lb. of m-tolualdehyde works out to 4.1 kw-hr (C.C.) assuming 40% overall current efficiency.

Examples

Manganese sulphate was prepared as described earlier. 400 c.c. of m-xylene was added at 40°C and the m-tolualdehyde was isolated by the sodium bisulphite treatment as described earlier. Weight of m-tolualdehyde obtained was 16 gms giving a current efficiency of 45%. The experiments were continued with the same electrolyte and in the second and third experiments 18 and 14.5 g respectively were obtained giving 40% and 36% current efficiency. In a second series of experiments, 15, 18 and 15 g of m-tolualdehyde were obtained, the current efficiency being 40%, 45% and 37.5% respectively.

4. Oxidation of mixed Xylenes and Mixed Aldehydes:

The method is similar to the oxidation of p-xylene as described earlier. The mixed xylenes supplied by Central Sewing Machine Co. was used and is a combination of meta and ortho xylene. Oxidation could be carried out at 35-50°C but preferably at 40°C.

Isolation of the Aldehydes

The method employed is quite similar to p-tolualdehyde and the overall current efficiency varies from 37 to 45%, taking all different cycles of operation. The energy consumption per lb. of the mixed aldehydes works out to 4.1 kw-hr (C.C.) assuming 40% overall current efficiency.

Examples

Manganese sulphate was prepared as described earlier under p-xylene oxidation. 400 c.c. of the mixed xylenes was added at 40°C and the mixed aldehydes were isolated by sodium bisulphite treatment as described earlier. Weight of mixed aldehydes was 15 gms giving a current efficiency of 45%. Subsequent runs with the same electrolyte gave a current efficiency of 40% and 35% respectively.

We claim:

1. A process for the preparation of (i) p-tolualdehyde (ii) o-tolualdehyde (iii) m-tolualdehyde (iv) mixed tolualdehydes, which consists in oxidizing the corresponding xylenes with manganese sulphate obtained by electrolytic oxidation of a paste of manganese sulphate in sulphuric acid as described in Patent No. 66728.

2. A process as claimed in claim 1 wherein the paste of manganese sulphate obtained from the electrolyte cell is allowed to react with ortho, meta, para xylenes and mixed xylenes by agitation in a separate reactor.

3. A process as claimed in claim 2 wherein the oxidation of p-xylene, o-xylene, m-xylene and mixed xylenes is carried out at 35°C, 30°C, 40°C, 50°C respectively.

4. A process as claimed in any of the preceding claims wherein 0.5 to 5 c.c. or more of the respective xylenes is taken for oxidation for every gram of manganese sulphate started with, but preferably about 1 c.c. per gram.
to isolate the aldehyde or by the steam distillation of the whole emulsion.

6. A process as claimed in any of the preceding claims wherein the process is made cyclic on a practical scale as follows: a paste of manganese sulphate in sulphuric acid is oxidized to manganous sulphate as mentioned in Claim 1; α-, β-, and γ-xylene and mixed xylenes are oxidized to o-toluic aldehyde, m-toluic aldehyde, p-toluic aldehyde and mixed toluiddehydes; aldehydes are isolated, volatile organic matter is removed from the manganous sulphate paste in sulphuric acid resulting after the oxidation and the manganese sulphate is reoxidized to manganic sulphate as hereinbefore described.

7. A process as claimed in any of the preceding claims wherein p-toluic aldehyde is prepared by oxidation of p-xylene by manganic sulphate according to the process as hereinbefore described.

8. A process as claimed in any of the preceding claims wherein o-toluic aldehyde is prepared by oxidation of o-xylene by manganic sulphate according to the process as hereinbefore described.

9. A process as claimed in any of the preceding claims wherein m-toluic aldehyde is prepared by oxidation of m-xylene by manganic sulphate according to the process as hereinbefore described.

10. A process as claimed in any of the preceding claims wherein mixed toluiddehydes are prepared by oxidation of mixed xylenes by manganic sulphate according to the process as hereinbefore described.

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Dated the 2nd day of August 1969.