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Specification No. 66175. Application No. 66175, 19th December 1958. Complete specification left on 27th August 1959. (Application Accepted 20th June 1960.)

A PROCESS FOR THE OXIDATION OF ORTHO, META AND PARA XYLENES AND MIXED XYLENES TO THE CORRESPONDING TOLUALDEHYDES.

### PROVISIONAL SPECIFICATION

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 describes the nature of this invention.

THIS IS AN INVENTION BY HANDADY VENKATAKRISHNA UDUPA, AND MYSORE SESHAIYER VENKATACHALAPATHI, ALL OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, ALL INDIAN SUBJECTS.

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 10-15% by passing current for nearly double the time that is theoretically required. It was also studied by Fichter and Stocker 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 55% sulphuric acid and oxidising it to manganic sulphate electrolytically as described in Patent No. 62379. The paste thus obtained is used to oxidise 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 making up to the required strength in acid is reoxidised to manganic 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 cyclic, the manganous sulphate and sulphuric acid being used for a number of experiments. *p*-Xylene is oxidised by manganic sulphate at 20 to 40°C but preferably at 30°C in a separate reactor in order to yield *p*-tolualdehyde with an overall current efficiency of 45 to 50%. *o*-Xylene is oxidised at 25-45°C but preferably at 35°C and *m*-xylene is oxidised at 35-50°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*-Tolualdehyde :

*p*-Xylene is treated with the paste of manganic sulphate obtained by the process described in the Patent No. 62379 in an agitator provided with a reflux condenser to prevent loss of *p*-xylene. Oxidation could be carried out at 20° to 45°C the duration of oxidation being reduced by increasing the temperature. But at higher temperatures, considerable resinification takes place leading to lower yields and the products are rather coloured. It is immaterial whether the *p*-xylene 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 0.5 cc or more *p*-xylene for every gram of manganous sulphate employed in the paste will have to be used but about 5 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 *p*-xylene and *p*-tolualdehyde are removed 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 colour 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 collected together. A wash with soda ash solution removes any *p*-toluic 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 *p*-tolyl carbinol, di-tolyl and any resin 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 soda ash or sulphuric acid and steam distilled. In the latter case the sulphur dioxide liberated could be absorbed to give further bisulphate. The aldehyde obtained in the steam distillate is separated, dried with anhydrous calcium chloride and distilled under vacuum to obtain *p*-tolualdehyde in the purest form.

The third procedure would be to treat the *p*-xylene layer, after removal of *p*-toluic acid, with a saturated solution of sodium bisulphite and the addition compound of the aldehyde is decomposed and distilled as above. The paste after separation of the *p*-xylene layer followed by (if necessary) an extraction with *p*-xylene is recycled to the electrolytic cell for regeneration of manganic sulphate as described in Patent No. 62379. The overall current efficiency for oxidation of *p*-xylenes 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

220 gms manganous sulphate was dissolved in 392 cc of water and 308 cc concentrated sulphuric acid was added with efficient stirring. This suspension was oxidised by passing 40 amp. hrs at 5 amp/dm<sup>2</sup> at 50-55°C using a rotating lead anode (1" diam. and anode area immersed being 1.2 dm<sup>2</sup>). The cell voltage was 3.6 to 3.8 volts. The current efficiency was 80%.

350 cc of *p*-xylene was added at 25°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 with the same electrolyte and in the second and third runs 18.5 and 16.5 g respectively were obtained giving 46.5 and 41.5% current efficiency. In a second series of experiments, 20, 18 and 16 g of *p*-tolualdehyde were obtained, the current efficiencies being 50%, 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 72 gms of *p*-tolualdehyde was obtained in four experiments giving an average current efficiency of 45%.

#### 2. Oxidation of *o*-Xylene to *o*-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 45°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 oxidation of *o*-xylene to *o*-tolualdehyde varies from 38 to 45% taking all different cycles of operation. The energy consumption per lb. of *o*-tolualdehyde works out to 4.1 kw.hr (D.C.) assuming 40% overall current efficiency.

#### Examples

Manganic sulphate was prepared as described earlier.

400 cc of *o*-xylene was added at 35°C and the *o*-tolualdehyde was isolated by the sodium bisulphite treatment as described earlier. Weight of *o*-tolualdehyde obtained was 18 gms. The current efficiency came to 45%. The experiment was continued with the same electrolyte and in the second and third experiments 16 and 15 g respectively were obtained giving 40% and 37.5% current efficiency. In a second series of experiments, 18, 16 and 15.5 g of *o*-tolualdehyde were obtained, the current efficiencies being 45%, 40% and 38.3% respectively.

Price : TWO RUPEES.

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

The procedure is quite analogous to p-xylene as described earlier and m-xylene is employed instead of p-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 36 to 40% taking all different cycles of operation. The energy consumption per lb. of m-tolualdehyde works out to 4.1 kw-hr (D.C.) assuming 40% overall current efficiency.

#### Examples

Manganic sulphate was prepared as described earlier.

400 cc 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 40%. The experiments were continued with the same electrolyte and in the second and third experiments 16 and 14.2 g respectively were obtained giving 40% and 36% current efficiency. In a second series of experiments, 16, 16 and 15 g of m-tolualdehyde 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 xylenes. Oxidation could be carried out at 35°-50° 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 (D.C.) assuming 40% overall current efficiency.

#### Examples

Manganic 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 18 gms giving a current efficiency of 45%. Subsequent runs with the same electrolyte gave a current efficiency of 40% and 38% respectively.

The following are among the noteworthy features of this invention :

(1) A process for the preparation of (i) p-tolualdehyde (ii) o-tolualdehyde (iii) m-tolualdehyde (iv) mixed tolualdehydes, which consists in oxidising the corresponding xylenes with manganic sulphate obtained by electrolytic oxidation of a paste of manganous sulphate in sulphuric acid as described in Patent No. 62379.

(2) A process as in (1) wherein the paste of manganic sulphate obtained from the electrolytic cell is allowed to react 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 excess corresponding xylenes either by fractional distillation or as bisulphite addition compound which is decomposed to isolate the aldehyde or by the steam distillation of the whole emulsion.

(6) A process as above wherein the process of oxidation of manganous to manganic sulphate, oxidation of o-, m-, and p-xylenes and mixed xylenes to o-tolualdehyde, m-tolualdehyde, p-tolualdehyde and mixed tolualdehydes and vacuum treatment of reactant for removal of volatile organic matter followed by reoxidation are made cyclic on a practical scale.

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

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

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

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

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Dated this 1st day of December 1958.

## COMPLETE SPECIFICATION.

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 VENKATAKRISHNA UPUPA, AND MYSORE SESHAIYER VENKATACHALAPATHI BOTH OF THE CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE, KARAIKUDI, MADRAS, INDIA, BOTH INDIAN CITIZENS.

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 10-15% by passing current for nearly double the time that is theoretically required. It was also studied by Fichter and Stocker 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 55% sulphuric acid and oxidising it to manganic sulphate electrolytically as described in Patent No. 62379. The paste thus obtained is used to oxidise 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 making up to the required strength in acid is reoxidised to manganic 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 cyclic, the manganous sulphate and sulphuric acid being used for a number of experiments.

p-Xylene is oxidised by manganic sulphate at 20 to 40°C but preferably at 30°C in a separate reactor in order to yield p-tolualdehyde with an overall current efficiency of 45 to 50%. o-Xylene is oxidised at 25-45°C but preferably at 35°C and m xylene is oxidised at 35-50°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-Tolualdehyde :

p-Xylene is treated with the paste of manganic sulphate obtained by the process described in the Patent No. 62379 in an agitator provided with a reflux condenser to prevent loss of p-xylene. Oxidation could be carried out at 20° to 45°C the duration of oxidation being reduced by increasing the temperature. But at higher temperatures, considerable resinifi-

cation takes place leading to lower yields and the products are rather coloured. It is immaterial whether the p-xylene 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 0.5 cc or more p-xylene for every gram of manganese sulphate employed in the paste will have to be used but about 5 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 p-xylene and p-tolualdehyde are removed 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 colour 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 collected together. A wash with soda ash solution removes any p-toluic 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 p-tolyl carbinol, di-tolyl and any resin 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 soda ash or sulphuric acid and steam distilled. In the latter case the sulphur dioxide liberated could be absorbed to give further bisulphite. The aldehyde obtained in the steam-distillate is separated, dried with anhydrous calcium chloride and distilled under vacuum to obtain p-tolualdehyde in the purest form.

The third procedure would be to treat the p-xylene layer, after removal of p-toluic acid, with a saturated solution of sodium bisulphite and the addition compound of the aldehyde is decomposed and distilled as above. The paste after separation of the p-xylene layer followed by (if necessary) an extraction with p-xylene is recycled to the electrolytic cell for regeneration of manganic sulphate as described in Patent No. 62379. 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*

220 gms manganous sulphate was dissolved in 392 cc of water and 308 cc concentrated sulphuric acid was added with efficient stirring. This suspension was oxidised by passing 40 amp. hrs at 5 amp/dm<sup>2</sup> at 50-55°C using a rotating lead anode (1" diam. and anode area immersed being 1.2 dm<sup>2</sup>). The cell voltage was 3.6 to 3.8 volts. The current efficiency was 80%.

350 cc of p-xylene was added at 25°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 with the same electrolyte and in the second and third runs 18.5 and 16.5 g respectively were obtained giving 46.5 and 41.5% current efficiency. In a second series of experiments, 20, 18 and 16 g of p-tolualdehyde were obtained, the current efficiencies being 50%, 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 72 gms of p-tolualdehyde was obtained in four experiments giving an average current efficiency of 45%.

#### *2. Oxidation of o-Xylene to o-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 45°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 oxidation of o-xylene to o-tolualdehyde varies from 38 to 45% taking all different cycles of operation. The energy consumption per lb. of o-tolualdehyde works out to 4.1 kw-hr (D.C.) assuming 40% overall current efficiency.

#### *Examples*

Manganic sulphate was prepared as described earlier.

400 cc of o-xylene was added at 35°C and the o-tolualdehyde was isolated by the sodium bisulphite treatment as described earlier. Weight of o-tolualdehyde obtained was 18 gms. The current efficiency came to 45%. The experiment was continued with the same electrolyte and in the second and third experiments 16 and 15 g respectively were obtained giving 40% and 37.5% current efficiency. In a second series of experiments, 18, 16 and 15.5 g of o-tolualdehyde were obtained, the current efficiencies being 45%, 40% and 38.3% respectively.

#### *3. Oxidation of m-Xylene to m-Tolualdehyde:*

The procedure is quite analogous to p-xylene as described earlier and m-xylene is employed instead of p-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 36 to 40% taking all different cycles of operation. The energy consumption per lb. of m-tolualdehyde works out to 4.1 kw-hr (D.C.) assuming 40% overall current efficiency.

#### *Examples*

Manganic sulphate was prepared as described earlier.

400 cc 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 40%. The experiments were continued with the same electrolyte and in the second and third experiments 16 and 14.2 g respectively were obtained giving 40% and 36% current efficiency. In a second series of experiments, 16, 16 and 15 g of m-tolualdehyde 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 xylenes. 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 (D.C.) assuming 40% overall current efficiency.

#### *Examples*

Manganic 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 18 gms giving a current efficiency of 45%. Subsequent runs with the same electrolyte gave a current efficiency of 40% and 38% 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 oxidising the corresponding xylenes with manganic sulphate obtained by electrolytic oxidation of a paste of manganous sulphate in sulphuric acid as described in Patent No. 62379.

2. A process as claimed in Claim 1 where the paste of manganic sulphate obtained from the electrolytic 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 25°, 30°, 40°C, 45°C respectively.

4. A process as claimed in any of the preceding claims 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 claimed in any of the preceding claims wherein the corresponding aldehyde formed is recovered from the excess corresponding xylenes either by fractional distillation or as bisulphite addition compound which is decomposed

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 manganous sulphate in sulphuric acid is oxidised to manganic sulphate as mentioned in Claim 1; o-, m-, and p-xylenes and mixed xylenes are oxidised to o-tolualdehyde, m-tolualdehyde, p-tolualdehyde and mixed tolualdehydes; aldehydes are isolated, volatile organic matter is removed from the manganous sulphate paste in sulphuric acid resulting after the oxidation and the manganous sulphate is reoxidised to manganic sulphate as hereinbefore described.

7. A process as claimed in any of the preceding claims wherein p-tolualdehyde 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-tolualdehyde 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-tolualdehyde 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 tolualdehydes are prepared by oxidation of mixed xylenes by manganic sulphate according to the process as hereinbefore described.

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*Dated this 22nd day of August 1959.*