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(54) PROCESS FOR THE PREPARATION OF AROMATIC DICARBOXYLIC ACIDS

(71) We, LABOFINA S.A. a Belgian Body Corporate, of 33 Rue de la Loi, 1040 Brussels, Belgium do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the preparation of aromatic dicarboxylic acids from dialkyl aromatic hydrocarbons, and more particularly to a process for producing terephthalic and isophthalic acids from p- and m-dialkylbenzenes.

The production of aromatic dicarboxylic acids by oxidation of dialkyl aromatic hydrocarbons, particularly of xylenes, in the liquid phase by molecular oxygen and in the presence of a heavy metal catalyst is a matter of considerable industrial importance which has been the subject of a tremendous amount of work over the past three decades. The major difficulty encountered when carrying out this operation results from the fact that, although xylenes are easily transformed into the corresponding toluic acids, the further oxidation of these acids is much more difficult and results in only negligible yield of dicarboxylic acids when ordinary catalytic methods are used. Numerous methods have been devised to overcome this difficulty, most of which consist in adding some activator or promoter. One of these methods comprises the use of a bromine-containing compound as activator and a lower fatty acid, e.g. acetic acid, as solvent. Although this method has reached full commercial fruition, it suffers serious drawbacks since the use of bromine at high temperature raises severe corrosion problems which can only be solved by the use of expensive construction materials such as Hastelloy C or titanium. "Hastelloy" is a registered Trade Mark. Moreover, under the strong oxidizing conditions applied in this process, the acetic acid

solvent is significantly consumed which results in additional costs.

To avoid those corrosion problems, other methods have been proposed which consist in using as activator, instead of bromine, an aldehydic and/or ketonic compound, e.g. acetaldehyde and/or methylethylketone. These methods require less severe conditions and, although acetic acid is still used as a solvent, conventional stainless steel equipment can be employed. However, the activator is consumed in the reaction, mainly by oxidation into acetic acid which is therefore a co-product of the reaction and must be separated, purified and sold for the process to be economically attractive. Still other methods have been proposed to avoid the drawbacks arising from the use of an extraneous compound as activator. For instance, it has been shown possible to oxidize in good yield p-xylene into terephthalic acid in an acetic acid medium containing only cobalt as catalyst but in exceedingly large amounts. Nevertheless, in this case also, a significant consumption of acetic acid takes place.

More recently, different methods have been claimed whereby p-xylene is oxidized into terephthalic acid in the absence of any solvent and activator. Temperatures higher or close to the melting point of p-toluic acid, i.e. 179°C, are used so as to achieve liquid-phase conditions. Although these methods appear remarkably simple in principle, they are difficult to apply in practice: without an activator, the intermediate p-toluic acid is rather refractory to oxidation and without solvent, technical problems associated with the handling of solids and with the removal of the heat generated during the reaction arise. For instance, the separation of terphthalic acid from the other components of the reaction mixture is a difficult task which is generally achieved by heating and washing treatments at elevated temperatures, e.g. at 230—270°C as disclosed in U.S. Patent 3,883,584 or even

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at 290—350°C as in U.S. Patent 3,711,539. Obviously, such treatments require the use of expensive pressure vessels made of corrosion-resistant material and should cause increased decomposition and discoloration of the reaction products.

Accordingly, the present invention provides a process for the preparation of aromatic dicarboxylic acids by oxidation of *p*- or *m*-dialkylbenzenes with molecular oxygen in the presence of catalytic amounts of at least one heavy metal salt, at a temperature of 140°C to 220°C, in which process the oxidation is performed in the presence of the *p*- or *m*-alkyl benzoic acid corresponding to the said *p*- or *m*-dialkylbenzene in such an amount that the molar ratio of aromatic monocarboxylic acid to dialkylbenzene is from 0.01 to 100:1 and in the presence of water which is used in such an amount that the molar ratio of water to aromatic monocarboxylic acid is from 0.4 to 60:1, at a pressure sufficient to maintain at least part of the water in the liquid phase at the reaction temperature.

The process of the present invention is applicable to dialkyl aromatic hydrocarbons, particularly *p*- and *m*-dialkylbenzenes having alkyl radicals which contain 1 to 4 carbon atoms. Typical starting materials include the para- and meta-isomers of xylene, methyl-ethylbenzene, diethylbenzene and cymene.

It is a well known fact that in the oxidation of organic compounds by molecular oxygen, the presence of water is generally not desirable and may even be detrimental. According to the most widespread opinion, water would interfere with the radical initiation processes of the reaction. For instance, in U.S. Patent 2,853,514 dealing with the oxidations of alkylbenzenes and more especially of *p*-xylene, it is stated that "the water concentration should be maintained at less than 3 molar in order to avoid an unreasonable prolonged induction period". Expressed in other terms, the water concentration should be maintained at less than about 5% by weight. It is only when a powerful radical-generating species such as bromine is present in the system that water may be tolerated in substantial amount. However, even in such cases, it appears that water is inherently detrimental for oxidation reactions. Thus, in U.S. Patent 3,139,459, wherein is disclosed a process for oxidizing *p*-xylene into terephthalic acid with a cobalt catalyst in the presence of HBr and of acetic acid as solvent, it is taught that "when an amount of water in excess of about 0.05 parts by weight per part of solvent (5 percent by weight) is allowed to accumulate, the

reaction is substantially stopped". Accordingly, in view of the prior art teachings, it is highly surprising that under the conditions of the present process not only may water be used in quantities in excess of 50 wt % or even more without prejudicing the reaction, but also, as shown hereinafter, water must be present in substantial amounts for the reaction to take place smoothly without induction or inhibition problems.

The amount of water to be used in the process of the present invention depends on different factors, mainly on temperature and the composition of the reaction mixture. Preferably, the amount of water will be sufficient for the monocarboxylic acid (toluic acid in the case of the oxidation of *p*- or *m*-xylene) to be substantially in solution at the working temperature. As the solubility of toluic acid in water steeply increases with temperature in the range considered here, the amount of water to be used may be lower as the temperature is higher. As a general rule, however, the molar amount of water will not be lower than 40 mole% based on monocarboxylic acid present in the reaction mixture. Although no upper limit strictly exists for the concentration of water which is by no means detrimental for the oxidation reaction, there is no advantage in using so large an amount of water that more than e.g. 10% of the benzenedicarboxylic acid present in the system is dissolved.

In the case of oxidation of *p*-xylene to terephthalic acid, water should not exceed a molar amount of $160,000 \cdot 10^{-9.0175 T}$ per mole of terephthalic acid, T being the working temperature in °C. It has been found that still other factors have to be taken into account. For example, when the amount of terephthalic acid in the system is relatively high, more especially when the molar ratio of terephthalic acid to *p*-toluic acid is higher than 2/3, the upper limit as defined hereinabove may be too high for the oxidation reaction to take place at a high rate. As a matter of fact, the presence of a too large amount of water with respect to *p*-toluic acid may affect adversely the reaction rate, especially when the amount of *p*-xylene in the system is relatively small as is the case when the reaction has reached an advanced stage. Advantageously, the amount of water should be lower than 60 moles per mole of *p*-toluic acid. In most cases, there is no advantage in using an amount of water substantially higher than 10 moles per mole of *p*-toluic acid which is present in the system.

The temperature at which the oxidation reaction has to be carried out is not critical either but, as a general rule, it is from 140 to 220°C, preferably from 140 to 200°C,

advantageously from 160 to 180°C. Below 140°C, the solubility of the monocarboxylic acid in water is so low that the amount of water to be used to place this monocarboxylic acid substantially in solution would be too high for the process to be economically attractive. On the other hand, working above 200°C generally results in increased overoxidation, undesirable side-reactions and corrosion problems.

The catalyst used in the process of the present invention may be a salt of any heavy metal conventionally employed in the oxidation of xylenes into benzenedicarboxylic acids provided that it is introduced in such a form that it can be dissolved in the reaction medium. Salts of lower aliphatic carboxylic acids, such as the acetates, propionates, butyrates, and also the naphthenates and toluates of cobalt and manganese and mixtures thereof are generally used. An effective amount of a co-catalyst may also be added to these salts.

When the dialkylbenzene substrate, water and the catalyst are brought into contact and heated at a temperature in the range as indicated, in the presence of molecular oxygen, active oxidation does not take place unless the corresponding monocarboxylic acid is also present in the system. This is surprising in view of the fact that the monocarboxylic acid is much less easily oxidized by molecular oxygen than the dialkylbenzene. Accordingly, it is an important aspect of the present invention that the monocarboxylic acid must at any time be present in the system in sufficient amount. The minimum amount of monocarboxylic acid is such that the molar ratio of monocarboxylic acid to dialkylbenzene is at least 0.01, preferably at least 0.1.

In carrying out the process of the present invention, the dialkylbenzene in admixture with the corresponding monocarboxylic acid and eventually other intermediate oxidation products is heated in the presence of water and the heavy-metal catalyst while an oxygen-containing gas is passed through the mixture. Efficient stirring is provided so as to ensure intimate contact between the different components. Active oxidation soon takes place as attested by an intense oxygen absorption and by a rapid increase of temperature. An important advantage of the present process is the ease with which temperature control can be achieved: owing to the presence of a substantial amount of water in the reaction mixture, the heat evolved from the highly exothermic oxidation can easily be removed by controlled evaporation of water.

As the reaction proceeds, i.e. as more

dialkylbenzene is transformed, oxygen absorption decreases and may even virtually cease if additional dialkylbenzene is not added into the system. Indeed, it is another important aspect of the present invention that to achieve active oxidation and high yields of benzenedicarboxylic acid sufficient dialkylbenzene must be present in the system for the molar ratio of monocarboxylic acid to dialkylbenzene not to become higher than 100. Accordingly, in the practice of the invention, fresh dialkylbenzene should be added to the reaction mixture at such a rate that this condition is fulfilled. This addition may be made continuously or intermittently. For instance, the reaction may be performed strictly in batch until oxygen absorption has virtually ceased. Then, the dicarboxylic acid can be separated by simple filtration at the reaction temperature. Indeed, it is an important practical advantage of the present process that the dicarboxylic acid formed in the reaction is present as relatively large crystals suspended in an aqueous medium containing the major part of the intermediate monocarboxylic acid. It can therefore be easily separated from the latter by filtration, centrifugation or any solid-liquid separation device at any temperature at which the monocarboxylic acid is still substantially in solution. The filtrate from this operation contains the catalyst in addition to substantially the whole of the intermediate oxidation products; it can therefore be recycled as such, together with fresh dialkylbenzene, to the oxidation zone for reprocessing.

According to another embodiment of the present invention, the process may be carried out as continuous flow process, for example in accordance with the scheme illustrated in the drawing accompanying the provisional specification, in which xylene is used as dialkylbenzene.

With reference to the drawing, the reaction is performed in an oxidizer 1, the residence time of the reactants being adjusted so that the prescribed concentrations of xylene and of toluic acid are maintained. Heat evolved in the reaction is removed by vaporizing water from the reaction mixture. Some xylene is vaporised azeotropically along with water and is separated in decanter 2 after condensation of the vapours. The oxidate from oxidizer 1 is transferred into stripper 3 where any unreacted xylene is removed by stripping with water. The dicarboxylic acid present as a precipitate in the effluent from stripper 3 is separated in separator 4 and washed in washer 5 with hot water which may at least in part come from decanter 2. The filtrate and washings are directly recycled to oxidizer 1. As those skilled in

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the art will appreciate, it is an especially advantageous feature of this process that water which is used as a washing solvent for the dicarboxylic acid may be heated and vapourised, at least in part, by the heat evolved in the oxidation itself, without need of an extraneous source of energy.

The present invention is illustrated by the following Examples.

Example 1

Into a 11 corrosion-resistant autoclave equipped with a mechanical agitation device, a heating jacket, a condenser, a gas inlet tube and a vent, there was charged:

p-xylene	100 g
p-toluic acid	180 g
water	150 g (or 630 mole % based on toluic acid).

Cobalt and manganese naphthenates to a concentration of 0.0250 M and 0.0025 M, respectively.

The amount of cobalt naphthenate was thus 7.5 millimoles and the amount of manganese naphthenate was 0.75 millimole.

The molar ratio of p-toluic acid to p-xylene was 1.4 and the molar ratio of water to p-toluic acid was 6.3.

The reactor was pressurised with air up to a pressure of 20 atmospheres and the above mixture was heated while stirring and admitting air at a flow rate of 300 litres per hour (measured at 20°C and atmospheric pressure). Oxygen absorption started as the temperature reached 140°C. The temperature then increased rapidly and was maintained at 185°C by controlled cooling. The oxygen absorption rate increased steeply during the first 30 minutes of reaction and then decreased progressively. After heating at 185°C for 285 minutes, 106 litres of oxygen were absorbed. The mixture was cooled and the autoclave was opened. The precipitate contained therein was filtered, washed with water and dried under vacuum at about 80°C. By analysis, it was shown to consist of 181 g of terephthalic acid, 118 g of toluic acid (which is considerably less than the amount charged initially), and 7 g of carboxybenzaldehyde. During the reaction, about 6 g of p-xylene had been entrained by the air flow.

A control experiment was carried out under the same conditions except that 157 g of p-xylene was substituted for the p-toluic acid charged in the autoclave. The volume of the charge was thus about the same but no toluic acid was present therein. Oxygen absorption only started when the

temperature reached 177°C and suddenly ceased after about 20 minutes of reaction. No terephthalic acid was detected in the reaction mixture. Still another control experiment was performed as described in the Example except that water was omitted. No oxygen absorption took place even after heating at 185°C for two hours. These control experiments clearly show the importance of having p-toluic acid and water present simultaneously in the charge for oxidizing p-xylene into terephthalic acid in accordance with the present invention.

Another comparative experiment was carried out under the same conditions except that the manganese naphthenate was omitted. Observable oxygen absorption started as hereinabove but suddenly fell off after about 80 minutes of reaction. Total oxygen absorption was limited to 58 litres and the amount of terephthalic acid in the reaction mixture was only 68 g. These results show the advantage of using at least a certain amount of manganese salt together with cobalt salt as catalyst for oxidizing p-xylene to terephthalic acid when the reaction is carried out in the presence of substantial amounts of water.

Example 2

The experiment of Example 1 was repeated except that the oxidation was discontinued after heating for about 180 minutes at 185°C. Then, the reaction mixture was discharged on a pressure filter at 185°C to separate terephthalic acid from the other oxidation products. The resulting cake was washed twice with water at 185°C and dried. After cooling at room temperature, the combined filtrate and washings were filtered to separate precipitated p-toluic acid which was also washed with water. The final filtrate, which contained substantially the whole of the catalysts, was concentrated by evaporation until its volume was the same as the volume of water initially charged into the autoclave. This concentrated solution was charged into the autoclave, together with the precipitate of p-toluic acid and the same amount of fresh p-xylene as in the original charge. The resulting mixture was then oxidized as already described. The same procedure was repeated nine times. Upon analysis it was concluded that the yield of the terephthalic acid produced in this series of operations was on the average higher than 87 mole % based on the amount of p-xylene reacted.

Example 3

Into the same autoclave as in Example 1, there was charged:

p-xylene 100 g
p-toluic acid 180 g
water 50 g
cobalt naphthenate 7.5 millimoles
(about 0.025 mole per litre of organic material).

p-xylene. Thus, in summary, the overall result of the operation is a transformation of p-xylene into terephthalic acid in the presence of an almost steady concentration of p-toluic acid.

Example 6

The same amounts of p-xylene, p-toluic acid and water as in Example 2 are charged into the autoclave together with 3.75 millimoles of each of cobalt and manganese naphthenates. The mixture is then oxidized by air under exactly the same conditions as in Example 2 except that the temperature is 170°C. instead of 185°C. After 230 minutes of reaction 174 litres of oxygen have been absorbed. The reaction mixture is then cooled, treated and analyzed as described in Example 1. It consists of 98 g of terephthalic acid, 179 g of p-toluic acid, 7 g of p-carboxy-benzaldehyde and some unreacted p-xylene.

Example 7

Under the conditions of the preceding Example, a series of 13 consecutive operations are carried out thereby recycling the catalysts and intermediates as described in Example 2. Terephthalic acid is obtained as white powder in an average yield of 87 mole percent. From a thorough analysis of the different streams, it is concluded that the remainder consists mainly of carbon dioxide, some p-tolualdehyde not recycled and some light acids. No formation of heavy by-products, tar or other coloured bodies is detected.

Example 8

The same amounts of p-xylene, p-toluic acid and water as in Example 1 are charged into the autoclave together with 3.9 millimoles of each cobalt and manganese acetates. The mixture is then oxidized by air under exactly the same conditions as in Example 1 except that the temperature is 165°C.

After 300 minutes of reaction, 61 litres of oxygen have been absorbed and upon analysis of the reaction mixture it is shown that 91 g of terephthalic acid have been formed.

This Example shows that by the process of the present invention p-xylene can be transformed into terephthalic acid at a temperature well below the melting point of p-toluic acid without resorting to the use of a lower fatty acid solvent.

Example 9

The following charge is heated while stirring and passing air thereinto at a flow rate of 300 litres per hour under a pressure of 20 atmospheres:

The molar ratios of p-toluic acid to p-xylene and of water to p-toluic acid were thus 1.4 and 2.1, respectively.

The reactor was pressurized with air up to a pressure of 20 atmospheres and the above mixture was heated while stirring and introducing air at a flow rate of 300 litres per hour (measured at 20°C and atmospheric pressure). Oxygen absorption started when the temperature was 100°C. The temperature then increased rapidly and was maintained at 185°C by controlled cooling. The oxygen absorption rate increased steeply during the first 20 minutes of the reaction and then decreased progressively. After 240 minutes of reaction, 101 litres of oxygen were absorbed. The reaction was then discontinued by cooling and the autoclave was opened. The precipitate contained therein was washed with water, filtered and dried under vacuum at about 80°C. The filtrate was treated with a cation-exchange resin to remove the metal catalysts and then evaporated to dryness.

The reaction mixture contained 137 g of terephthalic acid, 177 g of p-toluic acid and 7 g of p-carboxybenzaldehyde.

During the reaction, about 3 g of p-xylene were entrained by the air flow.

Example 4

The experiment of Example 1 is repeated except that 7.5 millimoles of manganese naphthenate are used as the sole catalyst. After 310 minutes of reaction, 95 litres of oxygen has been absorbed. The reaction mixture is then cooled, treated and analyzed as described in Example 1.

It consists of 150 g of terephthalic acid, 146 g of p-toluic acid and 7 g of p-carboxybenzaldehyde.

Example 5

The experiment of Example 2 is repeated except that 75 ml of water are charged into the autoclave and that 7.5 millimoles of manganese toluate are used as the sole catalyst. After 240 minutes of reaction 81 litres of oxygen have been absorbed. Upon analysis, the reaction mixture was shown to consist of 111 g of terephthalic acid, 179 g of p-toluic acid, i.e., almost the same amount as in the initial charge, 7 g of carboxybenzaldehyde and some unreacted

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p-xylene	68 g
p-toluic acid	120 g
water	250 g
cobalt naphthenate	2.5 millimoles
manganese naphthenate	10.0 millimoles

10 Thus, the water to p-toluic acid molar ratio is 15.7 instead of 6.3 as in most of the preceding Examples. Oxygen absorption starts when the temperature reaches about 125°C. The temperature is then maintained at 170°C. After 300 minutes of reaction, 43 litres of oxygen have been absorbed and the reaction is discontinued by cooling. The reaction mixture is then treated and analyzed as described in Example 1. It comprises 49 g of terephthalic acid, 139 g of p-toluic acid and 5 g of p-carboxybenzaldehyde.

20 This Example clearly shows that the oxidation of p-xylene into terephthalic acid can be carried out in the presence of very large amounts of water in accordance with the process of the present invention.

Example 10

25 The experiment of the preceding Example is repeated except that p-xylene is omitted and that manganese naphthenate is used as the sole catalyst. Only negligible absorption of oxygen is observed upon heating the mixture at 170°C for one hour. The temperature is then raised up to 185°C, but no change in the absorption rate takes place. After one hour at the latter temperature 50 ml of p-xylene are injected into the reactor. Evident oxygen absorption then suddenly starts and after 145 minutes amounts to 29 litres.

35 This Example shows that p-xylene must be present in the charge if p-toluic acid is to be oxidized into terephthalic acid in accordance with the process of the present invention.

Example 11

45 The following charge is heated while stirring and passing air thereinto at a flow rate of 200 litres per hour under a pressure of 20 atmospheres:

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p-xylene	155 g
p-toluic acid	10 g
water	50 g
cobalt naphthenate	2.5 millimoles
manganese naphthenate	2.5 millimoles

60 Thus, the molar ratios of p-toluic acid to p-xylene and of water to p-toluic acid are 0.05 and 38, respectively. Intense oxygen absorption starts when the temperature reaches 180° and amounts to 92 litres after 245 minutes at 185°C., when the reaction is discontinued by cooling. As is shown by analysis, the reaction mixture consists of 96

g of terephthalic acid, 108 g of p-toluic acid and 5 g of p-carboxybenzaldehyde.

A comparative experiment is carried out under the same conditions except that the p-toluic acid is omitted. No significant reaction takes place while heating the mixture for 4 hours at 185°C.

In another comparative experiment, 100 g of water are charged into the autoclave instead of 50 g. Therefore, the molar ratio of water to p-toluic acid is 76 instead of 38. Evident oxygen absorption starts as the temperature reaches 175°C. However, after about 75 minutes of reaction at 185°C., the oxygen absorption rate falls suddenly down to a negligible level. The total oxygen absorption is only 44 litres.

These comparative experiments show how important it is to have enough p-toluic acid relative to the amount of water in the system in order to be able to oxidize p-xylene into terephthalic acid according to the process of the present invention.

Example 12

The following charge is heated while passing air thereinto at a flow rate of 300 litres per hour under a pressure of 20 atmospheres:

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p-xylene	100 g
p-toluic acid	180 g
cobalt naphthenate	3.75 millimoles
manganese naphthenate	3.75 millimoles

It can be seen that this charge is the same as in the experiment of Example 6 except that water is omitted. Oxygen absorption starts as the temperature reaches about 160°C but falls rapidly to almost nil after an absorption of only 4.5 litres. Heating is continued for two hours at 185°C without any effect upon the reaction rate. Then 30 ml of water are injected into the reactor whereby intense oxygen absorption takes place abruptly. Heating at 185°C is still continued for 240 minutes before cooling the reaction mixture which is treated and analyzed as already described. It is thus determined that the reaction mixture consists of 143 g of terephthalic acid, 179 g of p-toluic acid and 7 g of p-carboxybenzaldehyde.

This Example shows that under the conditions of the present process water is not only not detrimental for the oxidation of p-xylene but exerts a beneficial effect upon the initiation thereof.

WHAT WE CLAIM IS:—

1. A process for the preparation of aromatic dicarboxylic acids by oxidation of p- or m-dialkylbenzenes with molecular oxygen in the presence of catalytic amounts of at least one heavy metal salt, at a

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	p-xylene	68 g
	p-toluic acid	120 g
	water	250 g
5	cobalt naphthenate	2.5 millimoles
	manganese naphthenate	10.0 millimoles

Thus, the water to p-toluic acid molar ratio is 15.7 instead of 6.3 as in most of the preceding Examples. Oxygen absorption starts when the temperature reaches about 125°C. The temperature is then maintained at 170°C. After 300 minutes of reaction, 43 litres of oxygen have been absorbed and the reaction is discontinued by cooling. The reaction mixture is then treated and analyzed as described in Example 1. It comprises 49 g of terephthalic acid, 139 g of p-toluic acid and 5 g of p-carboxybenzaldehyde.

This Example clearly shows that the oxidation of p-xylene into terephthalic acid can be carried out in the presence of very large amounts of water in accordance with the process of the present invention.

Example 10

The experiment of the preceding Example is repeated except that p-xylene is omitted and that manganese naphthenate is used as the sole catalyst. Only negligible absorption of oxygen is observed upon heating the mixture at 170°C for one hour. The temperature is then raised up to 185°C. but no change in the absorption rate takes place. After one hour at the latter temperature 50 ml of p-xylene are injected into the reactor. Evident oxygen absorption then suddenly starts and after 145 minutes amounts to 29 litres.

This Example shows that p-xylene must be present in the charge if p-toluic acid is to be oxidized into terephthalic acid in accordance with the process of the present invention.

Example 11

The following charge is heated while stirring and passing air thereinto at a flow rate of 200 litres per hour under a pressure of 20 atmospheres:

	p-xylene	155 g
	p-toluic acid	10 g
50	water	50 g
	cobalt naphthenate	2.5 millimoles
	manganese naphthenate	2.5 millimoles

Thus, the molar ratios of p-toluic acid to p-xylene and of water to p-toluic acid are 0.05 and 38, respectively. Intense oxygen absorption starts when the temperature reaches 180° and amounts to 92 litres after 245 minutes at 185°C., when the reaction is discontinued by cooling. As is shown by analysis, the reaction mixture consists of 96

g of terephthalic acid, 108 g of p-toluic acid and 5 g of p-carboxybenzaldehyde.

A comparative experiment is carried out under the same conditions except that the p-toluic acid is omitted. No significant reaction takes place while heating the mixture for 4 hours at 185°C.

In another comparative experiment, 100 g of water are charged into the autoclave instead of 50 g. Therefore, the molar ratio of water to p-toluic acid is 76 instead of 38. Evident oxygen absorption starts as the temperature reaches 175°C. However, after about 75 minutes of reaction at 185°C., the oxygen absorption rate falls suddenly down to a negligible level. The total oxygen absorption is only 44 litres.

These comparative experiments show how important it is to have enough p-toluic acid relative to the amount of water in the system in order to be able to oxidize p-xylene into terephthalic acid according to the process of the present invention.

Example 12

The following charge is heated while passing air thereinto at a flow rate of 300 litres per hour under a pressure of 20 atmospheres:

	p-xylene	100 g
	p-toluic acid	180 g
	cobalt naphthenate	3.75 millimoles
	manganese naphthenate	3.75 millimoles

It can be seen that this charge is the same as in the experiment of Example 6 except that water is omitted. Oxygen absorption starts as the temperature reaches about 160°C but falls rapidly to almost nil after an absorption of only 4.5 litres. Heating is continued for two hours at 185°C without any effect upon the reaction rate. Then 30 ml of water are injected into the reactor whereby intense oxygen absorption takes place abruptly. Heating at 185°C is still continued for 240 minutes before cooling the reaction mixture which is treated and analyzed as already described. It is thus determined that the reaction mixture consists of 143 g of terephthalic acid, 179 g of p-toluic acid and 7 g of p-carboxybenzaldehyde.

This Example shows that under the conditions of the present process water is not only not detrimental for the oxidation of p-xylene but exerts a beneficial effect upon the initiation thereof.

WHAT WE CLAIM IS:—

1. A process for the preparation of aromatic dicarboxylic acids by oxidation of *p*- or *m*-dialkylbenzenes with molecular oxygen in the presence of catalytic amounts of at least one heavy metal salt, at a



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- temperature of 140°C to 220°C, in which process the oxidation is performed in the presence of the *p*- or *m*-alkyl benzoic acid corresponding to the said *p*- or *m*-dialkylbenzene in such an amount that the molar ratio of aromatic monocarboxylic acid to dialkylbenzene is from 0.01 to 100:1, and in the presence of water which is used in such an amount that the molar ratio of water to aromatic monocarboxylic acid is from 0.4 to 60:1, at a pressure sufficient to maintain at least part of the water in the liquid phase at the reaction temperature.
2. A process according to Claim 1, wherein the heavy metal salt is a cobalt or manganese salt or a mixture thereof.
3. A process according to Claim 1 or 2, wherein the molar ratio of aromatic monocarboxylic acid to dialkylbenzene is from 0.1 to 100.
4. A process according to any one of the preceding claims, wherein the molar ratio of water to aromatic monocarboxylic acid is from 0.4 to 10.
5. A process according to any one of the preceding claims, wherein the aromatic dicarboxylic acid is terephthalic acid, the dialkylbenzene is *p*-xylene, and the aromatic monocarboxylic acid is *p*-toluic acid.
6. A process according to Claim 1 substantially as hereinbefore described with reference to the accompanying drawing.
7. A process according to Claim 1, substantially as described in Example 1 or Example 2.
8. A process according to Claim 1, substantially as described in any one of Examples 3 to 12.
9. An aromatic dicarboxylic acid when obtained by a process as claimed in Claim 1 or Claim 8.
10. An aromatic dicarboxylic acid when obtained by a process as claimed in any one of Claims 2 to 7.
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