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(71) Applicants: SAMSUNG GENERAL CHEMICALS CO., LTD. [KR/KR]; San 222-2, Dokgod-ri, Daesan-up, Seosan-gun, Chungcheongnam-do 352-870 (KR). JOINT-STOCK COMPANY OF RESEARCH AND DESIGN INSTITUTE OF MONOMERS(AO NIPIM) [RU/RU]; Prospect Lenina, 106A, Tula, 300600 (RU).

(72) Inventors: NAZIMOK, Vladimir Filippovich; Flat 53, Khalturina St., 138, Tula, 300034 (RU). GONCHAROVA, Nadezhada Nikolaevna; Flat 94, Block 1, Volodarskogo St., 82, Tula, 300057 (RU). YURJEV, Valerij Petrovich; Flat 36, Lejtejzina St., 12, Tula, 300034 (RU). MANZUROV, Vladimir Dmitrievich; Flat 59, Demonstratsii St., 77, Tula, 300034 (RU).

(74) Agent: YOON, Dong, Yol; 648-23, Yoksam-dong, Kangnam-ku, Seoul 135-080 (KR).

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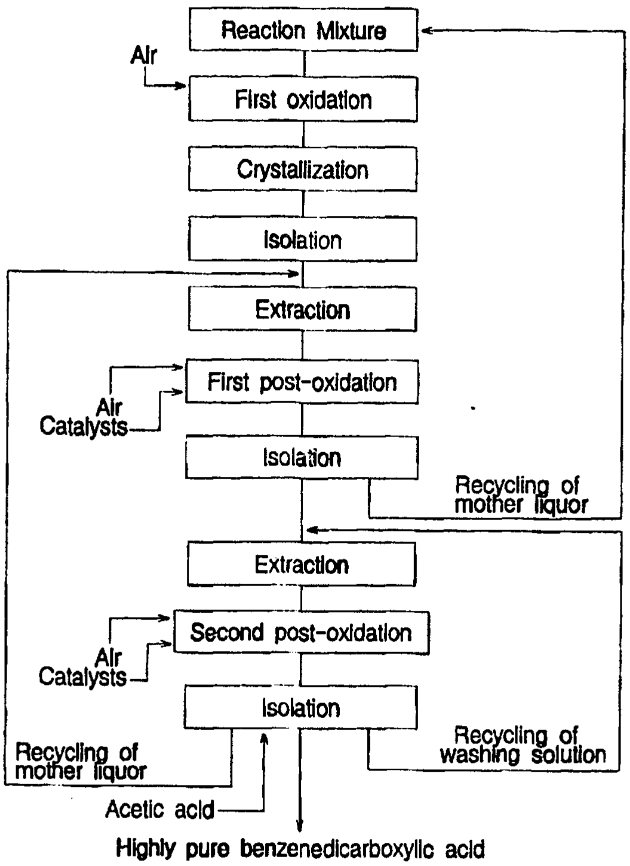
(54) Title: PRODUCTION METHOD OF HIGH PURITY ISOMERS OF BENZENEDICARBOXYLIC ACIDS

(57) Abstract

Disclosed herein is a process for producing highly purified benzenedicarboxylic acid isomers without an additional catalytic reductive purification step, which comprises (a) an oxidation step wherein xylene isomer is oxidized with molecular oxygen or molecular oxygen containing gas in the presence of a catalyst system composed of cobalt, manganese, bromine and at least one selected from nickel, chromium, zirconium and cerium in lower aliphatic carboxylic acid; and (b) an extraction/post-oxidation step wherein the oxidation product is crystallized to give cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2-80 °C lower than that of said heating, each of said oxidation and extraction/post-oxidation being carried out once or twice, provided that any one or both of said steps should be carried out twice. According to the invention, the solvent employed to extract impurities is recycled from the subsequent oxidation steps.



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PRODUCTION METHOD OF HIGH PURITY ISOMERS OF BENZENEDICARBOXYLIC ACIDS

Technical Field

The present invention relates to an organic synthesis, more particularly it relates to an improved process for producing highly purified benzenedicarboxylic acids isomers including terephthalic acid(TA), isophthalic acid(IA) and phthalic acid(PA), which are the most important monomers and semiproducts in a polymer chemistry for plastic, chemical fiber, film, varnishes and dyes.

Background Art

Terephthalic acid is useful as a starting material for producing polyester films and fibers and is commonly produced by the so-called SD process wherein paraxylene is oxidized with molecular oxygen in the presence of catalysts containing heavy metals in acetic acid solvent. However, since the terephthalic acid produced from the SD process contains high content (1000-3000ppm) of 4-carboxybenzaldehyde (hereinafter referred to as "4-CBA"), it is not a suitable starting material for producing polyester films and fibers.

Therefore, a method has been adopted in which terephthalic acid is reacted with methanol to form dimethyl terephthalate which is easily purified, and after purifying thereof, the dimethyl terephthalate is reacted with glycol to produce polyester. An alternative method which is more widely used for purifying terephthalic acid comprises the steps of dissolving the terephthalic acid in water at high temperature and pressure, treating the resulting solution with hydrogen over noble metal catalysts such as palladium in order to obtain highly purified terephthalic acid which contains less than 25ppm of 4-CBA. However, the known processes have drawbacks; the former method produces methanol during the preparation process of polyester and the latter method requires two separate plants, each for oxidizing and for purifying, since the conditions of oxidation and purification, for example solvent, catalysts and operation conditions are different from each other.

Up to now, several methods have been proposed to avoid difficulties involved in these conventional processes.

Methods for producing terephthalic acid without reductive purification step wherein paraxylene is oxidized with molecular oxygen via consecutive 4 steps in the presence of cobalt-manganese-bromine catalyst in acetic acid had been proposed.[USP 4772748, JP 62-270548A and JP 63-23982B] According to these methods, the paraxylene, in the first oxidation step, is oxidized at 180-230℃ for 40-150 minutes with the conversion of more than 95%; in the second oxidation step, is oxidized at a temperature of lower than that in the first reaction vessel by 2-30℃ for 20-90 minutes; in the third oxidation step, is oxidized at 235-290℃ for 10-60 minutes; and the final fourth oxidation step, is oxidized at 260℃. Since the TA produced by this method contains 0.027% of 4-CBA, it cannot be directly used for producing polyester fibers and films. Moreover, the above method has several disadvantages: a) since the high temperature (ca. 260℃) employed for oxidizing impurities in the third and fourth oxidation steps also causes oxidation of acetic acid solvent, the method is unfavorable in view of technology and economics; b) rather long reaction time in the first oxidation step decreases the efficiency of the process; and c) the content of 4-CBA contained in the TA as an impurity is still high(0.027%).

Accordingly, the above method is disadvantageous in that the efficiency of the process is relatively low and less purified TA is produced compared with the conventional method employing the reductive purification step.

Another method is proposed wherein paraxylene is oxidized with molecular oxygen in the presence of heavy metal compounds and a bromine compound in acetic acid medium with a conversion of higher than 90%, then the resulting mixture is crushed at 140-230℃ in the molecular oxygen atmosphere to reduce the average diameter of terephthalic acid particles by more than 20%(the first purification step) followed by the second step wherein the slurry obtained in the first purification step is oxidized with molecular oxygen at a temperature of at least 10℃ higher than that of the previous step and between 180 and 300℃.[JP 57-212881A] The method gives pure TA which can be directly employed for the polymerization.

However, the method requires a separate equipment for crushing the terephthalic acid, for example an agitator of high speed rotation. Moreover, it is difficult to produce highly pure terephthalic acid containing 4-CBA of less than 0.0025%.

Further, another method has been proposed wherein the crude product slurry produced by liquid phase catalytic oxidation of paraxylene is treated with molecular oxygen in acetic acid medium in the presence of catalyst composed of compounds of cobalt, manganese, chromium, cerium, lead or their mixtures, the amount of said catalyst being 0.01-5.0% by weight of TA to be purified.[Germany Pat. No. 1270030] The method is disadvantageous in that since the treatment is effected at a temperature as high as 250℃ for 1 hour, the acetic acid as well as impurities are oxidized.

Accordingly, there has been a need to provide an improved method for producing highly purified benzenedicarboxylic acid isomers without additional catalytic purification step.

Disclosure of Invention

Thus, an object of the invention is to provide a process for producing highly purified benzenedicarboxylic acid isomers without an additional catalytic reductive purification step, which comprises (a) an oxidation step wherein xylene isomer is oxidized with molecular oxygen or molecular oxygen containing gas in the presence of a catalyst system composed of cobalt, manganese, bromine and at least one selected from nickel, chromium, zirconium and cerium in a lower aliphatic carboxylic acid; and (b) an extraction/post-oxidation step wherein the oxidation product is crystallized to separate a cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding a lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating, each of said oxidation and extraction/post-oxidation steps being carried out once or twice, provided that any one or both of said steps should be carried out twice.

Another object of the invention is to provide a process for producing highly purified benzenedicarboxylic acid isomers without an additional catalytic reductive purification step, which comprises (a) the first oxidation step wherein xylene isomer is oxidized with molecular oxygen or molecular oxygen containing gas in the presence of a catalyst system composed of cobalt, manganese, bromine and at least one selected from nickel, chromium, zirconium and cerium in a lower aliphatic carboxylic acid; (b) the second oxidation step wherein the product obtained from the first oxidation step is reoxidized with said catalyst system; and (c) the first extraction/post-oxidation step wherein the product obtained from the second oxidation step is crystallized to separate a cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding a lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating.

Another object of the invention is to provide a process for producing highly purified benzenedicarboxylic acid isomers without an additional catalytic reductive purification step, which comprises (a) the first oxidation step wherein xylene isomer is oxidized with molecular oxygen or molecular oxygen containing gas in the presence of a catalyst system composed of cobalt, manganese, bromine and at least one selected from nickel, chromium, zirconium and cerium in a lower aliphatic carboxylic acid; (b) the second oxidation step wherein the product obtained from the first oxidation step is reoxidized with said catalyst system; (c) the first extraction/post-oxidation step wherein the product obtained from the second oxidation step is crystallized to separate cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding a lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating; and (d) the second extraction/post-oxidation step wherein the product obtained from the first extraction/post-oxidation step is crystallized to separate a cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding a lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating.

Another object of the invention is to provide a process for producing highly purified benzenedicarboxylic acid isomers without an additional catalytic reductive purification step, which comprises (a) the first oxidation step wherein xylene isomer is oxidized with molecular oxygen or molecular oxygen containing gas in the presence of a catalyst system composed of cobalt, manganese, bromine and at least one selected from nickel, chromium, zirconium and cerium in a lower aliphatic carboxylic acid; (b) the first extraction/post-oxidation step wherein the product obtained from the first oxidation step is crystallized to separate a cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding a lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating; and (c) the second extraction/post-oxidation step wherein the product obtained from the first extraction/post-oxidation step is crystallized to separate a cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding a lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating.

According to the process of the invention, an oxidation step wherein xylene isomer is oxidized with molecular oxygen or molecular oxygen containing gas in the presence of a catalyst system composed of cobalt, manganese, bromine and at least one selected from nickel, chromium, zirconium and cerium in a lower aliphatic carboxylic acid is carried out once or twice and an extraction/post-oxidation step wherein the oxidation product is crystallized to separate a cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding a lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system is carried out once or twice, provided that any one or both of said steps should be carried out twice.

The process according to the invention may be summarized as Method 1 wherein the oxidation step is carried out twice and the extraction/post-oxidation step is carried out once, Method 2 wherein the oxidation step is carried out twice and the extraction/post-oxidation step is carried out twice and Method 3 wherein the oxidation step is carried out once and the extraction/post-oxidation step is carried out twice.

The term "extraction/post-oxidation step" employed herein means that a process which consists of an extraction step wherein the product from the first or second oxidation step is crystallized to separate a cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding a lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent and an oxidation step wherein the slurry resulted from the extraction step is oxidized with a catalyst system. According to the invention, the catalyst system used in this oxidation step(post-oxidation step) is the same as that of used in the first or second oxidation step.

Hereinafter, the methods according to the invention shall be described in detail.

The xylene isomers used as a starting material in the methods of the present invention may include ortho-, metha- and para-isomers and these isomers give corresponding carboxybenzaldehydes(hereinafter referred to as "CBA") as impurities in the oxidation step. Thus, if para-, metha- or ortho-xylene is employed as a starting material, 4-CBA, 3-CBA or 2-CBA is respectively produced.

In accordance with the process of the invention, a reaction mixture composed of xylene isomer, lower aliphatic carboxylic acid and catalysts is preheated to a temperature of higher than

150℃ and lower than the temperature of the first oxidation reaction and then is introduced into the first oxidation reaction vessel at a linear velocity of 6-30m/s in a counter direction to the direction of revolution of the fluid in the reaction vessel.

The oxidation reaction is carried out in a lower aliphatic carboxylic acid by using molecular oxygen or a molecular oxygen containing gas at 150-230℃ for about 20-60 minutes in the presence of a cataylst system composed of cobalt-manganese-bromine and one or more selected from nickel, chromium, zirconium and cerium.

As molecular oxygen or molecular oxygen containing gas employed in the present invention, oxygen or air is employed, and a mixture of air and the vent gas resulted from the first oxidation is employed in the second oxidation or in the first or second extraction/post-oxidation.

As a lower aliphatic carboxylic acid employed as a medium as well as an extracton solvent in the process of the present invention, there may be included an aliphatic acid containing 1 to 6 carbon atoms, for example acetic acid, butanoic acid, pentanoic acid or hexanoic acid, and acetic acid is preferred.

The catalyst system employed according to the invention essentially consists of cobalt, manganese and bromine, and further comprises one or more heavy metals selected from nickel, chromium, zirconium or cerium. The example of cobalt compounds may include, not intended to be limited thereto, cobalt acetate or coblat naphthenate. The example of manganese compounds may include, not intended to be limited thereto, manganese acetate or manganese naphthenate. The example of bromine compounds may include, not intended to be limited thereto, sodium bromide or tetrabromoethane, or a mixture of bromine compounds and chlorine compounds in a ratio of 1 : 0.001 - 0.5 in terms of bromine and chlorine. The chlorine compounds may include, not intended to be limited thereto, $ZrOCl_2$, $NiCl_2 \cdot 6H_2O$ or hydrochloric acid, and may be added per se or in a salt form with zirconium or nickel which is employed as a component of catalyst system.

The heavy metal employed as a component of the catalyst system according to the invention may be in the form of any salt which can be dissolved in a lower aliphatic carboxylic acid, particularly acetic acid, and preferably is in the form of acetate. The ratio of each components of the catalyst varies according to the each oxidation steps as illustrated hereinafter.

In the case where the oxidation step is carried out twice, the slurry obtained from the first oxidation step is oxidized for 10 - 30 minutes by using the catalyst system same as that used in the first oxidation, a vent-gas from the first oxidation reactor, air and a reflux resulted from the crystallization step after the second oxidation.

In the extraction/post-oxidation step, the solvent contained in the slurry is replaced with new solvent followed by heating(Extraction step). The heating is carried out in order to extract impurities contained in the slurry. After heating, the slurry containing the extracted impurities is cooled and oxidized with the same catalyst system as that used in the oxidation step.(Post-oxidation step) The extraction/post-oxidation may be carried out once or twice.

The exraction/post-oxidation step according to the invention will be described in more detail as follows.

In the extraction/post-oxidation process, the slurry of crude benzenedicarboxylic acid isomers obtained from the first or second oxidation step is isolated to give a cake and the cake is reslurried with the lower aliphatic carboxylic acid which is obtained in isolating or washing the cake from the slurry resulted from the extraction/post-oxidation step. After reslurrying, the resulting slurry is treated under heating to a temperature of 200-280℃ for 5-60 minutes to extract the toluic acid and CBA contained in the benzenedicarboxylic acid isomer crystals as impurities. In this case, the aliphatic carboxylic acid recycled from the isolating or washing step to reslurry the cake should be used in such an amount that more than 60% of the lower aliphatic carboxylic acid contained in the slurry from the previous oxidation step can be replaced with.

Thus obtained impurities-containing slurry from the extraction by heating is subjected to oxidation by using the catalyst system and molecular oxygen containing gas at a temperature which is lower 2-80℃ than that of the extraction for 10-30 minutes and the resulting slurry is isolated and washed.

The above extraction/post-oxidation step can be effected once or twice and consequently the composition and concentration of the catalyst system, the source from which the lower aliphatic carboxylic acid which is used for reslurrying and the concentration of the impurity contained in the crude benzenedicarboxylic acid obtained from each oxidation step vary. However, in any cases, highly purified benzenedicarboxylic acid which contains less than 0.0025% of carboxybenzaldehyde is finally produced and for this purpose at least one or both of the oxidation and extraction/post-oxidation steps should be effected twice.

The reaction conditions of the above-mentioned Methods 1, 2, and 3 will be explained in more detail as follows.

In Method 1, the catalyst system employed in the post-oxidation step has a ratio of [Mt], a concentration of heavy metal added to cobalt-manganese-bromine component to [Co+Mn], a concentration of cobalt plus manganese of 1 : 0.01-0.2 and the total concentraion of heavy metal(s) added is 50-300ppm. The concentration of heavy metals employed in the fisrt oxidation : second oxidation : first extraction/post-oxidation is 1 : 0.5-0.9 : 0.05-0.20. The solvent for reslurrying the cake from the second oxidation step is recycled from the washing step for washing the cake resulted from the first extraction/post-oxidation step. The recycled solvent should be used in such an amount that at least 60% of the lower carboxylic acid contained in the slurry from the second oxidation step can be replaced with.

Where Method 1 is employed for producing highly pure benzenedicarboxylic acid, the concentration of CBA as an impurity contained in the crude benzenedicarboxylic acids produced from the first oxidation, second oxidation and first extraction/post-oxidation is 0.06-0.16%, 0.03-0.08% and less than 0.0025%, respectively.

In Method 2, the ratio of [Co+Mn] to [Mt] is 1 : 0.01-0.2 and the total concentraion of heavy metal(s) added is 30-200ppm. The concentration of heavy metal(s) employed in the fisrt oxidation : second oxidation : first extraction/post-oxidation : second extraction/post-oxidation is 1 : 0.5-0.9 : 0.1-0.3 : 0.05-0.2. The solvent for reslurrying the cake from the second oxidation step is recycled from the isolating step for isolating the cake from the slurry obtained in the second extraction/post-oxidation step. The recycled solvent should be used in such an amount that at least 60% of the lower carboxylic acid contained in the slurry from the second oxidation step can be replaced with. The solvent for reslurrying the cake from the first extraction/post-oxidation step is recycled from the washing step for washing the cake resulted from the second extraction/post-oxidation step. The recycled solvent should be used in such an amount that at least 60% of the lower carboxylic acid contained in the slurry from the first extraction/post-oxidation step can be replaced with. The above-explained recycling of the solvent to extract the impurity improves the efficiency of the solvent usage and thus make it possible to minimize the loss of solvent.

Where Method 2 is employed for producing highly pure benzenedicarboxylic acid, the concentration of CBA as an impurity contained in the crude benzenedicarboxylic acids produced from the first oxidation, second oxidation, first extraction/post-oxidation and second extraction/post-oxidation is 0.1-0.4%, 0.05-0.15%, 0.01-0.03% and less than 0.0025%, respectively.

In Method 3, the ratio of [Co+Mn] to [Mt] is 1 : 0.01-0.2 and the total concentraion of heavy metal(s) added is 40-300ppm. The concentration of heavy metal(s) employed in the first oxidation : first extraction/post-oxidation : second extraction/post-oxidation is 1 : 0.05-0.5 : 0.05-0.2. The solvent for reslurrying the cake from the first oxidation step is recycled from the isolating step for isolating the cake from the slurry obtained in the second extraction/post-oxidation step. The recycled solvent should be used in such an amount that at least 60% of the lower carboxylic acid contained in the slurry from the first oxidation step can be replaced with. The solvent for reslurrying the cake from the first extraction/post-oxidation step is recycled from the washing step for washing the cake resulted from the second extraction/post-oxidation step. The recycled solvent should be used in such an amount that at least 60% of the lower carboxylic acid contained in the slurry from the first extraction/post-oxidation step can be replaced with.

Where Method 3 is employed for producing highly pure benzenedicarboxylic acid, the concentration of CBA as impurity contained in the crude benzenedicarboxylic acids produced from the first oxidation, first extraction/post-oxidation and second extraction/post-oxidation is 0.04-0.15%, 0.01-0.05% and less than 0.0025%, respectively.

It is possible to make choice of the above Method 1, 2 or 3 in consideration of a cost for installation and a loss of reactant and solvent. That is to say, for example, when it is desired to lower the cost for installation, Method 1 wherein the concentraton of the catalyst employed is relatively high may be preferably chosen and when it is desired to reduce the loss of xylene isomers and lower aliphatic carboxylic acid by oxidation, Method 2 wherein the oxidation step is carried out under the mild conditions may be preferably chosen. Further, it is preferable to choose Method 3, where the moderate cost and loss of the reactant and solvent is required.

The main features and advantages of the present invention are as follows:

1) The extraction/post-oxidation step wherein the recycled solvent is employed to extract impurities under heating makes it possible to selectively oxidize the impurities while does not cause oxidation of solvent.

2) In the process for preparing benzenedicarboxylic acid comprising three or four oxidation steps in total, it is possible to selectively oxidize benzenedicarboxylic acid isomers at a moderate temperature with high yield by using an appropriate concentration of an improved catalyst system composed of cobalt, manganese and bromine together with one or more additional metals selected from nickel, chromium, zirconium and cerium in each oxidation step so that the rate limiting oxidation step in which toluic acid isomers and CBA are oxidized to benzenedicarboxylic acid can be accelerated while the side reaction which produces a high molecular weight colored organic compounds can be avoided.

3) The new method of introducing the reaction mixture into the reactor at high linear velocity of 6-30m/s provides rapid and almost homogeneous distribution of the reaction mixture over the reaction zone. And the preliminary heating of the reaction mixture to a temperature between 150℃ and oxidation reaction temperature can eliminate the temperature gradient in the reaction zone and provides a steady reaction proceeding over the entire reaction volume in combination with the rapid mixing of the reaction mixture. This also makes it possible to reduce the loss of lower aliphatic carboxylic acid used as a solvent

due to oxidation thereof.

These features and advantages of the present invention make it possible to produce highly purified benzenedicarboxylic acid isomer having color index of not more than 10°H and containing less than 0.0025% of CBA isomer, a principal impurity, while minimizing the loss of solvent.

Brief Description of Drawings

Fig. 1 shows a flow chart of the process according to the invention wherein the oxidation step is carried out twice and then the extraction/post-oxidation step is carried out once.(Method 1)

Fig. 2 shows a flow chart of the process according to the invention wherein the oxidation step is carried out twice and then the extraction/post-oxidation step is carried out twice.(Method 2)

Fig. 3 shows a flow chart of the process according to the invention wherein the oxidation step is carried out once and the extraction/post-oxidation step is carried out twice.(Method 3)

Best Mode for Carrying Out the Invention

The present invention will be explained more in detail by way of the following non-limitative Examples. In Examples, all the metals are employed in the form of acetate and the bromine is in the form of hydrobromic acid, and the "%" is by weight unless otherwise indicated.

Examples 1 to 9 and Comparative Examples 1 to 7

(Mehtod 1: oxidation step is carried out twice and then extraction/post-oxidation step is carried out once)

Example 1

A reaction mixture was prepared in a vessel made of titanium, which is equipped with an agitator and a heating jacket. The composition of the reaction mixture was 17% of p-xylene(1734kg), 80.63% of acetic acid, 2% of water, 732ppm of cobalt, 588ppm of manganese, 70ppm of nickel and 2270ppm of bromine.

The reaction mixture was fed into the heater using a centrifugal pump and heated to 160℃. The preheated mixture was introduced at a linear rate of 20m/s through 4 nozzles into the oxidation reactor($V=10m^3$) equipped with two parallel turbine agitators installed on a common shaft. The oxidation was effected at 198℃ and 18 kg/cm^2 for 40 minutes.

The product from the first oxidation was fed into the second oxidation reactor and treated with the reflux from the crystallizer connected to the second oxidation reactor and a mixture of a vent gas from the first oxidation reactor and air. During the second oxidation, the water concentration was maintained at 10%. The purity of terephthalic acid obtained after the second oxidation was improved to 1.9 and 1.3 times in terms of content of 4-CBA and color index, respectively, compared with those of the product from the first oxidation.

The reaction mixture to be supplied to the first extraction/post-oxidation was prepared in a vessel equiped with a stirrer. The cake isolated from the product of the second oxidation, which has 15% of residual solvent, was introduced into the reactor and subjected to extraction of the impurities contained therein with a solvent. As the solvent for extraction, one which is recycled from the washing step for washing the cake obtained from the first extraction/post-oxidation step is used. The amount of the solvent recycled is such an amount that 85% of the total solvent contained in the product of the second oxidation is replaced with. The resulting slurry contained 25% of terephthalic acid.

The slurry was fed to the heater to heat up to about 230 ℃ and then sent to a vessel equipped with a stirrer and could maintain a constant temperature, where the slurry was maintained for 10 minutes(The first extraction). And the heat-treated slurry was fed to the first extraction/post-oxidation reactor where the slurry was treated with a mixture of the vent-gas from the first oxidation reactor and air at 200℃, and at the same time a hydrobromic acid/acetic acid solution composed of cobalt, manganese, nickel, 95% of acetic acid, 4.875% of water and 0.125% of hydrobromic acid was fed to the reactor(The first post-oxidation). Finally, the composition of the reaction mixture in the first extraction/post-oxidation was 20% of terephthalic acid, 7% of water, 132ppm of [Co+Mn+Ni] and 212ppm of bromine.

The reaction time of the first post-oxidation was 20 minutes. After completion of the reaction, the product was crystallized at 105℃ under the atmospheric pressure in a collector. The solids were isolated by centrifugation, washed with fresh acetic acid and dried. The final product from the post-oxidation step contained 25ppm of 4-CBA and had a color index of 8°H. The yield was 98%. The total oxidation time from the first oxidation to the first extracton/post-oxidation was 80 minutes.

According to the process of the invention, the very rapid introduction of the reaction mixture into the reactor makes it possible to attain a rapid homogeneous distribution of the temperature and concentration of the reactants in the reactor and the use of the specific catalysts as well as the adoption of the extraction step using the recycled solvent make it possible to selectively oxidize specific compounds to produce highly pure phthalic acid isomers containing not more than 25ppm of CBA isomer and having less than 10°H of color index and to proceed with the process rapidly. The each step can be completed within about 10 to 40 minutes.

The oxidation conditions and results in Example 1 are shown in Table 1.

Example 2

The procedure of Example 1 was repeated except that 40 ppm of Ni, 20 ppm of Cr, 30 ppm of Zr and 40 ppm of Ce were employed instead of 70ppm of Ni and the reaction times and temperatures were changed as shown in Table 1. The finally produced terephthalic acid contained 15 ppm of 4-CBA and had the color index of 4°H. The oxidation conditions and results in Example 2 are shown in Table 1.

Example 3

The procedure of Example 1 was repeated except that 120 ppm of Zr was employed instead of 70ppm of Ni and the reaction times and temperatures were changed as shown in Table 1. The finally produced terephthalic acid contained 24 ppm of 4-CBA and had the color index of 8°H. The oxidation conditions and results in Example 3 are shown in Table 1.

Example 4

The procedure of Example 1 was repeated except that 120 ppm of Ce was employed instead of 70ppm of Ni and the reaction times and temperatures were changed as shown in Table 1. The finally produced terephthalic acid contained 22 ppm of 4-CBA and had the color index of 7°H. The oxidation conditions and results in Example 4 are shown in Table 1.

Example 5

The procedure of Example 1 was repeated except that the amount of the nickel was increased to 100 ppm from 70ppm and the reaction times and temperatures were changed as shown in Table 1. The finally produced terephthalic acid contained 20 ppm of 4-CBA and had the color index of 7°H. The oxidation conditions and results in Example 5 are shown in Table 1.

Comparative Example 1

The procedure of Example 1 was repeated except that no Ni was added and the reaction times and temperatures were changed as shown in Table 1. The finally produced terephthalic acid contained 25 ppm of 4-CBA and had high color index of 46°H. The oxidation conditions and results in Comparative Example 1 are shown in Table 1.

Comparative Example 2

The procedure of Comparative Example 1 was repeated except that the introduction rate of the reaction mixture was reduced from 28m/s to 1m/s and the extraction time was changed from 10 minutes to 1 minute. The finally produced terephthalic acid contained 650ppm of 4-CBA and had the color index of 26°H. The oxidation conditions and results in Comparative Example 2 are shown in Table 1.

Comparative Example 3

The procedure of Example 5 was repeated except that 50 ppm of Ni and 50 ppm of Cr were employed instead of 100ppm of Ni and the catalyst concentration, [Co+Mn+Ni+Cr] in the first post-oxidation reaction and bromine concentration were changed from 132ppm and 212ppm to 21ppm and 32ppm, respectively. The finally produced terephthalic acid contained 15 ppm of 4-CBA and had the color index of 4°H. The oxidation conditions and results in Comparative Example 3 are shown in Table 1.

Comparative Example 4

The procedure of Example 1 was repeated except that no Ni was added and the temperature of introducing the reaction mixture and the heating and reaction temperatures in the first extraction/post-oxidation were changed from 160℃, 230℃ and 200℃ to 60℃, 180℃ and 180℃, respectively. The finally produced terephthalic acid contained 222 ppm of 4-CBA and had the color index of 21°H. The oxidation conditions and results in Comparative Example 4 are shown in Table 1.

Example 6

The procedure of Example 1 was repeated except that m-xylene was employed instead of p-xylene. The finally produced isophthalic acid contained 15 ppm of 3-CBA and had the color index of 10°H. The oxidation conditions and results in Example 6 are shown in Table 1.

Comparative Example 5

The procedure of Example 6 was repeated except that no Ni was added, the linear velocity of introducing the reaction mixture was reduced from 20m/s to 1m/s and the holding time in the first extraction step was reduced from 10 minutes to 3 minutes. The finally produced isophthalic acid contained 160 ppm of 3-CBA and had the color index of 48°H. The oxidation conditions and results in Comparative Example 5 are shown in Table 1.

Example 7

The procedure of Example 1 was repeated except that o-xylene was employed instead of p-xylene and 40 ppm of Ni, 20 ppm of Cr, 30 ppm of Zr and 40 ppm of Ce were employed instead of 70ppm of Ni. The finally produced phthalic acid contained 20 ppm of 2-CBA and had the color index of 10°H. The oxidation conditions and results in Example 7 are shown in Table 1.

Comparative Example 6

The procedure of Example 1 was repeated except that p-xylene was replaced with o-xylene and the rate of introducing the reaction mixture was reduced from 20m/s to 1m/s. The finally produced phthalic acid contained 28 ppm of 2-CBA and had the color index of 20°H. The oxidation conditions and results in Comparative Example 6 are shown in Table 1.

Examples 8 to 17 and Comparative Examples 7 to 8

(Mehtod 2: oxidation step is carried out twice and then extraction/post-oxidation step is carried out twice)

Example 8

In this Example, a continuous unit consisting of a reaction mixture collector, a metering pump, reactor equipped with an agitator, a condenser and a crystallizer was employed to oxidize p-xylene. A reaction mixture of which composition was 14% of p-xylene(330g), 83.9% of acetic acid, 2% of water, 254ppm of cobalt, 127ppm of manganese, 23ppm of zirconium and 632ppm of bromine was introduced into the reaction mixture collector..

The reaction mixture was preliminarily heated to 160℃ and then fed into the reactor(1*l*) whilst supplying air thereto. The mixture was reacted at 192℃ while monitoring the contents of the gas, i.e., O_2, CO or CO_2, temperature, pressure, and the consumption rates of reaction mixture and air and sampling the reaction product at an appropriate interval. The samples were separated to liquid and solid phases and analyzed quantatively and qualitively using common techniques such as chromatography, polarography and photometric methods.

After completion of the first oxidation, the slurry resulted from the first oxidation was fed into the second oxidation reactor and treated at 185℃ with the air and the vent-gas from the first oxidation reactor and the reflux from the crystallizer connected to the second oxidation reactor. The second oxidation product was isolated to give a cake which was reslurried with the mother liquor recycled from the isolation step for isolating the cake from the slurry obtained from the second extraction/post-oxidation and then fed into the first extraction/post-oxidation reactor. The contents in the first extraction/post-oxidation reactor was heated to 230℃, maintained for 7 minutes and cooled to 198℃, and then was subjected to oxidation reaction. The concentration of the catalyst used in the oxidation was 5 times lower than that of the catalyst used in the first oxidation. After the first extraction/post-oxidation step, the concentration of CBA contained in the product terephthalic acid reduced from 950ppm(after the second oxidation) to 210ppm and the color index reduced from 9 °H to 7 °H.

The cake isolated from the first extraction/post-oxidation product was reslurried with the acetic acid recycled from the washing step for washing the cake isolated from the second extraction/post-oxidation and then fed into the second extraction/post-oxidation reactor. The contents in the second extraction/post-oxidation reactor was heated to 230℃, maintained for 7 minutes and cooled to 198℃, and then was subjected to oxidation reaction. The concentration of the catalyst used in the second post-oxidation was 10 times lower than that of the catalyst used in the first oxidation. The second post-oxidation product was cooled and terephthalic acid was isolated therefrom and washed with fresh acetic acid. The oxidation conditions and results in Example 9 are shown in Table 2.

In this Example, highly purified terephthalic acid containing 14ppm of 4-CBA and having a color index of 6°H can be produced.

<u>Example 9</u>

The procedure of Example 8 was repeated except that zirconyl chloride was employed instead of zirconyl bromide. The change of the zirconium compound from zirconyl bromide to zirconyl chloride produced no change in the color index of the produced terephthalic acid, but the content of 4-CBA was reduced from 14ppm to 11ppm. The oxidation conditions and results in Example 9 are shown in Table 2.

<u>Example 10</u>

The procedure of Example 8 was repeated except that nickel chloride hexahydrate was employed instead of zirconium bromide. When comparing with the result of Example 8, the content of 4-CBA was similar thereto and the color index of the produced terephthalic acid was lower. The oxidation conditions and results in Example 10 are shown in Table 2.

<u>Example 11</u>

The procedure of Example 8 was repeated except that cerium compound was employed instead of zirconium compound. Highly purified terephthalic acid was obtained. The oxidation conditions and results in Example 11 are shown in Table 2.

Example 12

The procedure of Example 8 was repeated except that chromium compound was employed instead of zirconium compound. Highly purified terephthalic acid was obtained. The oxidation conditions and results in Example 12 are shown in Table 2.

Example 13

The procedure of Example 8 was repeated except that a mixture of zirconium, nickel and chromium compounds was employed instead of zirconium compound. When comparing with the result of Example 8, the content of 4-CBA and the color index of the produced terephthalic acid was lowered. The oxidation conditions and results in Example 13 are shown in Table 2.

Comparative Example 7

The procedure of Example 13 was repeated except that no heavy metal was added. The quality of the produced terephthalic acid did not comply with the requirement of high purity. The oxidation conditions and results in Comparative Example 7 are shown in Table 2.

Examples 14 and 15

The procedure of Example 8 was repeated except that the capacity of the reactor was changed from $1l$ to $10m^3$. The reactor is equipped with two parallel agitators and a nozzle for controlling the rate and direction of introduction of the mixture. The first and second oxidations were carried out at the same temperature in Example 8 and the first and second post-oxidations were carried out at 188-199℃. The concentration of the catalyst was increased to about 2 times in Example 14 and about 1.5 times in Example 15 compared with Example 8. As results, highly purified terephthalic acids containing 10ppm and 24ppm, respectively were obtained. The oxidation conditions and results in Examples 14 and 15 are shown in Table 2.

Comparative Example 8

The procedure of Example 14 was repeated except that the reaction mixture was fed at a rate of 5m/s through 4 branch pipes instead of using a nozzle and reaction temperatures and times were changed as shown in Table 2. The color index of the produced terephthalic acid contained was as high as 28°H. The oxidation conditions and results in Comparative Example 8 are shown in Table 2.

Examples 16 and 17

The procedure of Example 8 was repeated except that m-xylene and o-xylene were oxidized in stead of p-xylene, respectively, and nickel was employed instead of zirconium. As results, highly purified terephthalic and isophthalic acids containing 12ppm and 23ppm of CBA and having color index of 6°H and 10°H, respectively were obtained. The oxidation conditions and results in Examples 16 and 17 are shown in Table 2.

Examples 18 to 20

(Mehtod 3: oxidation step is carried out once and then extraction/post-oxidation step is carried out twice)

Example 18

In this Example, p-xylene was oxidized in accordance with Method 3. A reaction mixture of which composition was 14% of p-xylene(378g), 83.8% of acetic acid, 2% of water, 618ppm of cobalt, 292ppm of manganese, 61ppm of nickel and 1416ppm of bromine was introduced into the reaction mixture collector.

The reaction mixture was preliminarily heated to 160℃ and then continuously fed into the reactor whilst supplying air thereto. The mixture was reacted at 188℃ while monitoring the contents of the gas, i.e., O_2, CO or CO_2, temperature, pressure, and the consumption rates of reaction mixture and air and sampling the reaction product at an appropriate interval. The samples were separated into liquid and solid phases and analyzed quantatively and qualitively using common techniques such as chromatography, polarography and photometric methods.

After completion of the first oxidation, the slurry resulted from the first oxidation was cooled to 100℃ to give cake, which was reslurried with the mother liquor recycled from the isolation step for isolating the cake from the slurry obtained from the second extraction/post-oxidation and then fed into the first extraction/post-oxidation reactor. The contents in the first extraction/post-oxidation reactor was heated to 240℃, maintained for 15 minutes and cooled to 198℃ followed by subjecting to oxidation reaction. The concentrations of the heavy metals and bromine in the catalyst used in the oxidation were 7 times and 9 times lower than those of the catalyst used in the first oxidation.

The cake isolated from the first extraction/post-oxidation product was reslurried with the acetic acid recycled from the washing step for washing the cake isolated from the second extraction/post-oxidation and then fed into the second extraction/post-oxidation reactor. The contents in the second extraction/post-oxidation reactor was heated to 240℃, maintained for 15 minutes and cooled to 198℃ followed by subjecting to oxidation. The concentration of the catalyst used in the second post-oxidation was 10 times lower than that of the catalyst used in the first oxidation. The second post-oxidation product was cooled and terephthalic acid was isolated therefrom and washed with fresh acetic acid. The oxidation conditions and results in Example 18 are shown in Table 3.

Example 19

The procedure of Example 18 was repeated except that the catalysts recovered from the mother liquor of the first oxidation was used instead of fresh catalysts. As a result, there could be obtained a highly purified terephthalic acid. The oxidation conditions and results in Example 19 are shown in Table 3.

Example 20

The procedure of Example 18 was repeated except that

31ppm of nickel and 31ppm of zirconium were employed instead of 61ppm of nickel. And the concentration of the catalyst used in the first and second post-oxidations were reduced to 8 times and 12 times, respectively, compared with those of in the first oxidation. As a result, there could be obtained a highly purified terephthalic acid. The oxidation conditions and results in Example 20 are shown in Table 3.

Table 1.

Example	First oxidation							Second Oxidation		First extraction/post-oxidation				Results	
	Catalyst conc. (ppm)				Oxidation conditions			Oxidation conditions		Extraction conditions		Oxidation conditions		Quality	
No.	Co	Mn	Mt	Br	Temp. T(℃)	Time t(min)	W* m/s	Temp. T(℃)	Time t(min)	Temp. T(℃)	Time t(min)	Temp. T(℃)	Time t(min)	CBA (ppm)	Color (°H)
Ex. 1	732	588	Ni70	2270	198	40	20	180	20	230	10	200	20	25	8
Ex. 2	700	580	Ni40 Cr20 Zr30 Ce40	2270	198	35	20	190	20	230	10	200	20	15	4
Ex. 3	700	580	Zr120	2270	198	35	20	185	20	230	10	200	20	24	8
Ex. 4	700	580	Ce120	2270	198	35	20	185	20	230	10	200	20	22	7
Ex. 5	950	550	Ni100	2500	200	35	16	195	18	210	25	188	22	20	7
C. Ex. 1	700	580	-	2270	198	35	28	180	20	230	10	200	20	25	46
C. Ex. 2	700	580	-	2270	198	35	1.0	180	20	230	1.0	200	20	650	26
C. Ex. 3	950	550	Ni50 Cr50	2500	186	35	9	180	60	230	10	200	60	421	9
C. Ex. 4	732	588	-	2270	218	35	20	180	20	180	10	180	60	222	21
Ex. 6	732	588	Ni70	2270	198	40	20	180	20	230	10	200	20	15	10
C. Ex. 5	710	580	-	2270	198	35	1.0	180	20	230	3.0	200	20	160	48
Ex. 7	700	580	Ni40 Cr20 Zr30 Ce40	2270	198	35	20	190	20	230	20	200	20	20	20
C. Ex. 6	732	588	Ni70	2270	198	40	1.0	180	20	230	10	200	20	28	20

W* : Linear velocity of introducing reaction mixture

Table 2.

Example No.	First oxidation							Second oxidation		First extraction/post-oxidation				Second extraction/post-oxidation				Results	
	Catalyst conc. (ppm)				Oxidation conditions			Oxidation conditions		Extraction conditions		Oxidation conditions		Extraction conditions		Oxidation conditions		Quality	
	Co	Mn	Mt	Br/Cl	Temp. T(℃)	Time t(min)	W* m/s	Temp. T(℃)	Time t(min)	Temp. T(℃)	Time t(min)	Temp. T(℃)	Time t(min)	Temp. T(℃)	Time t(min)	Temp. T(℃)	Time t(min)	CBA (ppm)	Color (°H)
Ex. 8	254	127	Zr23	632/-	192	38	12	185	20	230	7	198	20	230	7	198	20	14	6
Ex. 9	254	127	Zr23	612/28	192	38	12	185	20	230	7	198	20	230	7	198	20	11	5
Ex. 10	254	127	Ni24	612/35	200	38	12	185	20	240	7	200	20	240	7	200	20	18	3.5
Ex. 11	254	127	Ce24	632/-	192	38	12	185	20	230	7	198	20	230	7	198	20	23	6
Ex. 12	254	127	Cr24	632/-	192	38	12	185	20	230	7	198	20	230	7	198	20	25	5
Ex. 13	254	127	Zr12 Ni6 Cr6	632/-	192	38	12	185	20	230	7	198	20	230	7	198	20	10	3.5
C.Ex.7	254	127	-	632/-	192	38	12	185	20	230	7	198	20	230	7	198	20	60	7
Ex. 14	500	250	Ni45	920/-	192	40	18	185	18	225	10	198	15	225	5	188	15	10	4
Ex. 15	400	200	Ni38	640/-	192	40	16	185	20	230	5	188	20	230	12	199	18	24	5
C.Ex.8	500	250	Ni45	920/-	192	40	5	185	18	225	10	198	15	225	5	188	15	32	28
Ex. 16	254	127	Ni24	612/-	200	40	12	185	20	240	7	200	20	225	5	188	15	12	6
Ex. 17	254	127	Ni24	810/8	200	48	12	185	25	225	6	200	26	225	5	190	22	23	10

W* : Linear velocity of introducing reaction mixture

Table 3.

Example No.	First oxidation							First extraction/post-oxidation				Second extraction/post-oxidation				Results	
	Catalyst conc. (ppm)				Oxidation conditions			Extraction conditions		Oxidation conditions		Extraction conditions		Oxidation conditions		Quality	
	Co	Mn	Mt	Br	Temp. T(℃)	Time t(min)	W* m/s	Temp. T(℃)	Time t(min)	Temp. T(℃)	Time t(min)	Temp. T(℃)	Time t(min)	Temp. T(℃)	Time t(min)	CBA (ppm)	Color (°H)
Ex. 18	618	292	Ni61	1416	188	52	12	240	15	180	25	240	15	198	25	6	8
Ex. 19	618	292	Ni61	1416	192	52	12	230	15	185	25	235	15	198	20	6	8
Ex. 20	618	292	Ni31 Zr31	1114 116	192	46	12	240	15	185	25	240	8	198	20	5	7

W* : Linear velocity of introducing reaction mixture

Claims

1. A process for producing highly purified benzenedicarboxylic acid isomers without an additional catalytic reductive purification step, which comprises (a) an oxidation step wherein xylene isomer is oxidized with molecular oxygen or molecular oxygen containing gas in the presence of a catalyst system composed of cobalt, manganese, bromine and at least one selected from nickel, chromium, zirconium and cerium in lower aliphatic carboxylic acid; and (b) an extraction/post-oxidation step wherein the oxidation product is crystallized to give cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating, each of said oxidation and extraction/post-oxidation being carried out once or twice, provided that any one or both of said steps should be carried out twice.

2. The process according to Claim 1 characterized in that which comprises (a) the first oxidation step wherein xylene isomer is oxidized with molecular oxygen or molecular oxygen containing gas in the presence of a catalyst system composed of cobalt, manganese, bromine and at least one selected from nickel, chromium, zirconium and cerium in lower aliphatic carboxylic acid; (b) the second oxidation step wherein the product obtained from the first oxidation step is reoxidized with

said catalyst system; and (c) the first extraction/post-oxidation step wherein the product obtained from the second oxidation step is crystallized to give a cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating.

3. The process according to Claim 1 characterized in that which comprises (a) the first oxidation step wherein xylene isomer is oxidized with molecular oxygen or molecular oxygen containing gas in the presence of a catalyst system composed of cobalt, manganese, bromine and at least one selected from nickel, chromium, zirconium and cerium in lower aliphatic carboxylic acid; (b) the second oxidation step wherein the product obtained from the first oxidation step is reoxidized with said catalyst system; (c) the first extraction/post-oxidation step wherein the product obtained from the second oxidation step is crystallized to give cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating; and (d) the second extraction/post-oxidation step wherein the product obtained from the first extraction/post-oxidation step is crystallized to give a cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding lower aliphatic

carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating.

4. The process according to Claim 1 characterized in that which comprises (a) the first oxidation step wherein xylene isomer is oxidized with molecular oxygen or molecular oxygen containing gas in the presence of a catalyst system composed of cobalt, manganese, bromine and at least one selected from nickel, chromium, zirconium and cerium in lower aliphatic carboxylic acid; (b) the first extraction/post-oxidation step wherein the product obtained from the first oxidation step is crystallized to give cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating; and (c) the second extraction/post-oxidation step wherein the product obtained from the first extraction/post-oxidation step is crystallized to give cake of crude benzenedicarboxylic acid isomer, the cake is reslurried by adding lower aliphatic carboxylic acid solvent thereto followed by heating in order to extract impurities contained therein into the solvent, and the resulting slurry is oxidized with said catalyst system at a temperature of 2 - 80℃ lower than that of said heating.

5. The process according to any one of Claims 1 to 4, wherein

the reaction mixture to be introduced into the first oxidation reactor is preliminarily heated to a temperature between 150℃ and that of the first oxidation step.

6. The process according to Claim 2, wherein the lower aliphatic carboxylic acid solvent to reslurry the cake isolated from the second oxidation product is recycled from the washing step for washing the cake isolated from the first extraction/post-oxidation product.

7. The process according to Claim 3, wherein the lower aliphatic carboxylic acid solvent employed to reslurry the cake isolated from the second oxidation product is recycled from the isolation step for isolating the cake from the slurry obained from the second extraction/post-oxidation step and the lower aliphatic carboxylic acid solvent employed to reslurry the cake isolated from the first extraction/post-oxidation product is recycled from the washing step for washing the cake isolated from the second extraction/post-oxidation product.

8. The process according to Claim 4, wherein the lower aliphatic carboxylic acid solvent employed to reslurry the cake isolated from the first oxidation product is recycled from the isolation step for isolating the cake from the slurry obained from the second extraction/post-oxidation step and the lower aliphatic carboxylic acid solvent employed to reslurry the cake isolated from the first extraction/post-oxidation product is recycled from the washing step for washing the cake isolated from the second extraction/post-oxidation product.

9. The process according to Claim 2 or 3, wherein the first and second oxidation are carried out at 150-230℃ for 20-60 minutes.

10. The process according to Claim 4, wherein the first oxidation is carried out at 150-230℃ for 20-60 minutes.

11. The process according to any one of Claims 2 to 4, wherein the reaction mixture is fed into the first oxidation reactor at a linear velocity of 6-30m/s in a counter direction to the revolution direction of the contents in the reactor.

12. The process according to Claim 2, wherein the ratio of the concentration of the heavy metals selected from nickel, chromium, zirconium and cerium to the total concentration of cobalt and manganese is 0.01-0.2 : 1 and the total concentration of said heavy metals is 50-300ppm.

13. The process according to Claim 2, wherein the ratio of the concentration of the heavy metals selected from nickel, chromium, zirconium and cerium employed in the first oxidation, second oxidation and first post-oxidation is 1 : 0.5-0.9 : 0.05-0.2.

14. The process according to Claim 3, wherein the ratio of the concentration of the heavy metals selected from nickel, chromium, zirconium and cerium to the total concentration of cobalt and manganese is 0.01-0.2 : 1 and the total concentration of said heavy metals is 30-200ppm.

15. The process according to Claim 3, wherein the ratio of the concentration of the heavy metals selected from nickel, chromium, zirconium and cerium employed in the first oxidation, second oxidation, first post-oxidation and second oxidation is 1 : 0.5-0.9 : 0.1-0.3 : 0.05-0.2.

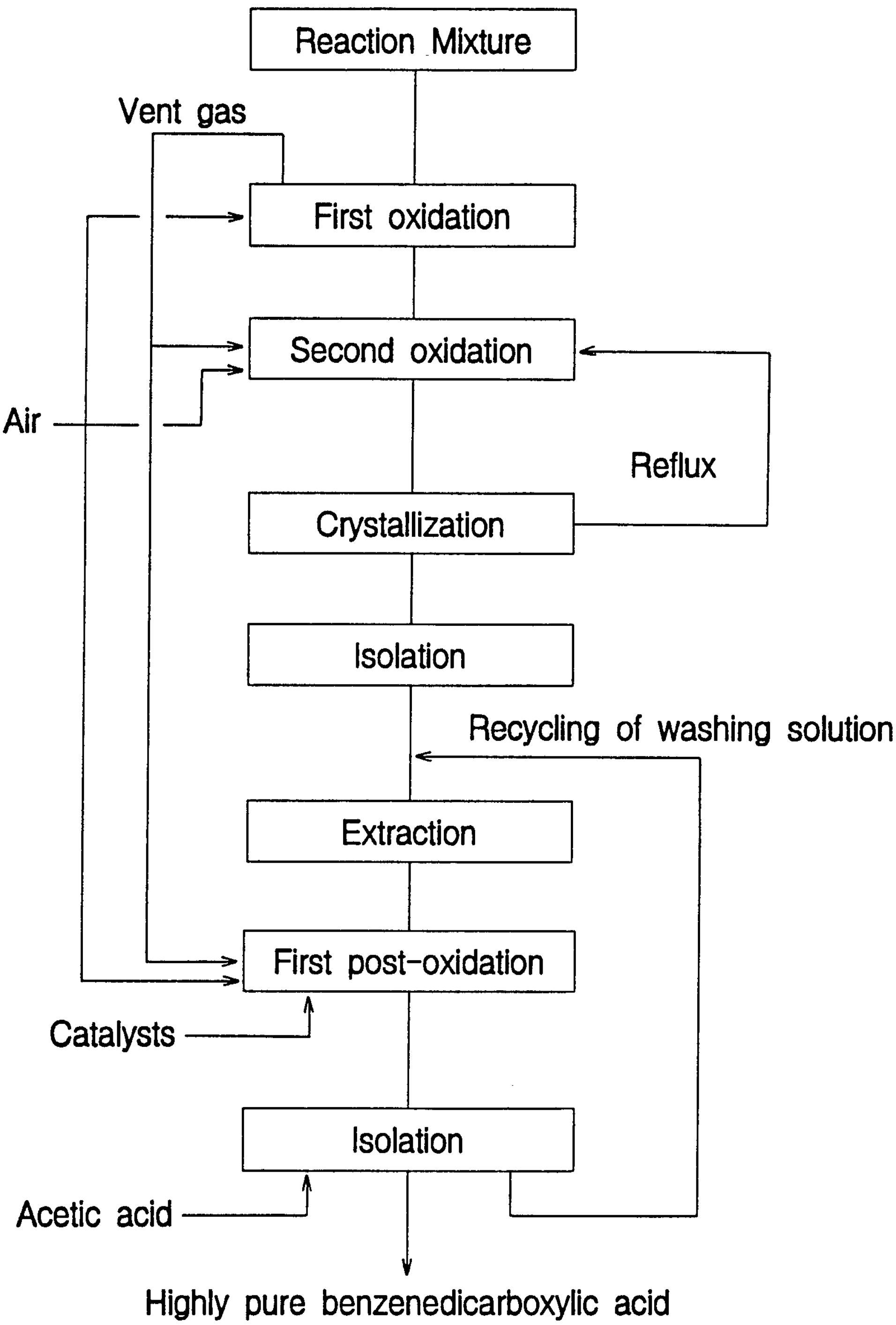
16. The process according to Claim 4, wherein the ratio of the concentration of the heavy metals selected from nickel, chromium, zirconium and cerium to the total concentration of cobalt and manganese is 0.01-0.2 : 1 and the total concentration of said heavy metals is 40-300ppm.

17. The process according to Claim 4, wherein the ratio of the concentration of the heavy metals selected from nickel, chromium, zirconium and cerium employed in the first oxidation, second oxidation and first post-oxidation is 1 : 0.05-0.5 : 0.05-0.2.

18. The process according to Claim 1, wherein the bromine compound is a bromine compound alone or a mixture of bromine compound and chlorine compound in a ratio of 1 : 0.001-0.5 in terms of bromine and chlorine.

19. The process according to any one of Claims 6 to 8, wherein the amount of the recycled lower carboxylic acid is such an amount that at least 60% of the lower carboxylic acid contained in the slurry from the previous oxidation step can be replaced with.

Fig 1.



Reaction Mixture
Vent gas
First oxidation
Second oxidation
Air
Reflux
Crystallization
Isolation
Recycling of washing solution
Extraction
First post-oxidation
Catalysts
Isolation
Acetic acid
Highly pure benzenedicarboxylic acid

Fig 2.

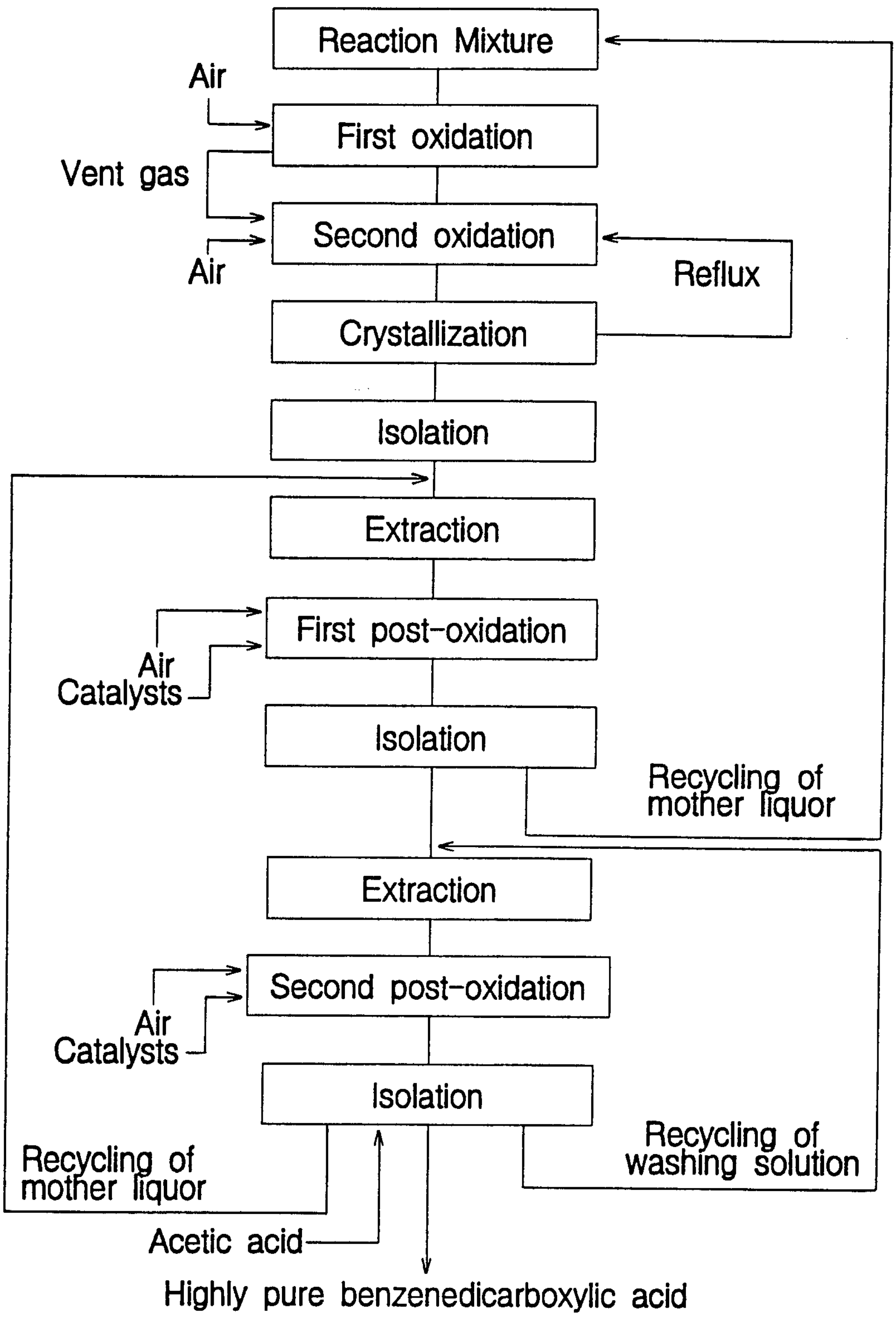
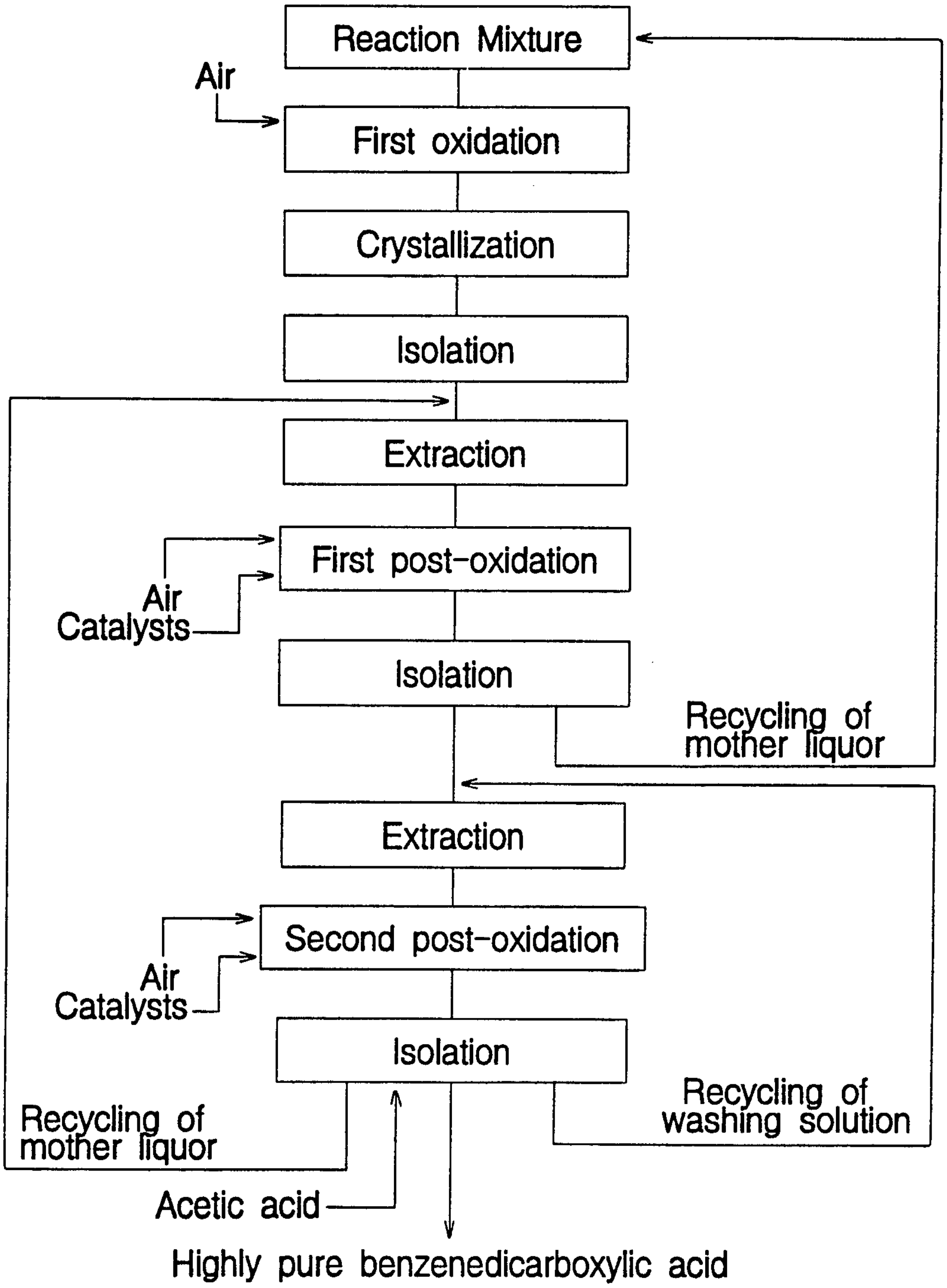

Reaction Mixture
Air
First oxidation
Vent gas
Second oxidation
Air
Reflux
Crystallization
Isolation
Extraction
First post-oxidation
Air
Catalysts
Isolation
Recycling of mother liquor
Extraction
Second post-oxidation
Air
Catalysts
Isolation
Recycling of mother liquor
Recycling of washing solution
Acetic acid
Highly pure benzenedicarboxylic acid

Fig 3.


Reaction Mixture
Air
First oxidation
Crystallization
Isolation
Extraction
First post-oxidation
Air
Catalysts
Isolation
Recycling of mother liquor
Extraction
Second post-oxidation
Air
Catalysts
Isolation
Recycling of mother liquor
Recycling of washing solution
Acetic acid
Highly pure benzenedicarboxylic acid

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 93/00106

A. CLASSIFICATION OF SUBJECT MATTER

IPC^5: C 07 C 63/26, 51/265

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC^5: C 07 C 63/00, 51/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4 772 748 (H. HASHIZUME et al.) 20 September 1988 (20.09.88), examples; claims.	1,9,10,12,18
A	US, A, 4 877 900 (A. TAMARU et al.) 31 October 1989 (31.10.89), examples; claims.	1,9,10,12,18
A	US, A, 3 683 017 (J.W. AGER) 08 August 1972 (08.08.72), totality.	1,12,14,16,18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 May 1994 (17.05.94)	14 June 1994 (14.06.94)

Name and mailing address of the ISA/ AT	Authorized officer
AUSTRIAN PATENT OFFICE Kohlmarkt 8-10 A-1014 Vienna Facsimile No. 1/53424/535	Hofbauer e.h. Telephone No. 1/5337058/26

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