This invention relates to a process for recovering benzene polycarboxylic acids from mixtures of poly-substituted benzenes having all substituents selected from the group consisting of -COOH, -CONH₂ and -COONH₄. In particular, this invention relates to a process for recovering essentially nitrogen-free phthalic acids from mixtures of the ammonium salts and amides of the acids.

Copingend application of William G. Toland, Jr., Serial No. 371,209, filed July 30, 1953, now Patent No. 2,722,549, describes a process for oxidizing aliphatic hydrocarbons, such as the three xylene isomers, toluene, and the like, by heating the aliphatic hydrocarbons with ammonium sulfate, a sulfide such as hydrogen sulfide or ammonium sulfide and water to a temperature from about 550° F. to the critical temperature of water under a superatmospheric pressure sufficient to maintain a part of the water in liquid phase. In a representative operation, 1 mol of xylene, 1.83 mols of ammonium sulfate, 0.18 mols of ammonium sulfide and 30 mols of water are heated to about 620° F. under a pressure of 2800 p.s.i.g. for approximately 2 hours. 97% conversion of the xylene is achieved and a yield of phthalic acid derivatives amounting to 91% of theory is obtained. The reaction product produced in this oxidation process is a mixture of ammonium phthalates and phthalic acid amides. Three types of compound are present having the formulas:

Φ(COOH)NH₂, Φ(COONH₂) and NH₂OC≡COONH₄

Thus, the reaction product contains diammonium phthalate, diamid of phthalic acid and the half-salt half-amide of phthalic acid. In the reaction product from about 60 to 80% of the total potential acid groups is in the form of the ammonium salt and the remainder is in the form of the amide, i.e., 60 to 80% of the side chains of the reaction product is ammonium carboxylate -COONH₄ while the remainder is amide -CONH₂, constituting a nitrogen content of 14 to 17% by weight.

While the oxidation process above referred to is characterized by high conversions of xylene and high yields of phthalic acid values, the recovery of phthalic acid having the degree of purity required in most commercial uses from the crude oxidation reaction product is difficult. A phthalic acid product satisfactory for virtually any commercial use must have a nitrogen content calculated as ammonia below about 0.1% by weight and for a great many uses, for example, in the production of alkyl resins, it is necessary that the nitrogen content calculated as ammonia be below 0.03% by weight. These low nitrogen contents are not easily attained. They can be reached by saponifying the ammonium salt-amide product with caustic to produce a solution of sodium phthalates from which phthalic acids are precipitated by the addition of acid. This method involves substantial consumption of caustic and sulfuric acid which considerably increases the ultimate cost of the phthalic acid product. It has been found also that the hydrolysis can be accomplished in a strongly acid medium, i.e., 2 mols of sulfuric acid per mol of phthalic acid contained in the salt-amide mixture at high temperature. This method, however, is attended by extraordinarily high corrosion rates with the most corrosion resistant materials now available requiring frequent replacement of expensive equipment with attendant reduction in the operating factor of the process.

It is an object of this invention to provide a method whereby mixtures of poly-substituted benzene having essentially all substituents selected from the group consisting of -COOH, -CONH₂ and -COONH₄ can be converted to essentially nitrogen-free benzene polycarboxylic acid.

It is another object of this invention to provide a method whereby mixtures of ammonium salts and amides of phthalic acids can be quantitatively and essentially converted to essentially nitrogen-free phthalic acids.

These objects are obtained pursuant to the invention by heating the poly-substituted benzene in the presence of an aromatic monocarboxylic acid, preferably benzoic or toluic acid, and preferably present in molar excess, at a temperature of 400 to 600°F. to produce the desired benzene polycarboxylic acid and a nitrile product such as benzonitrile or toluene which is continuously removed as a vapor. The preferred excess of molten benzoic or toluic acid provides a convenient medium for the reaction and also shifts the equilibrium of the reaction in favor of the desired benzene polycarboxylic acid. When the reaction has been completed by the continuous removal of the nitrile product, the benzene polycarboxylic acid is separated from solution in the excess of molten benzoic or toluic acid by cooling the solution to crystallize out the benzene polycarboxylic acid which is removed by filtration.

Example 1

Isophthalic acid is produced pursuant to the invention in the following manner. 1 molar part of a mixture of diammonium isophthalate, diamid of isophthalic acid and the half-salt half-amide of isophthalic acid containing about 15% by weight of nitrogen is mixed with 4 molar parts of toluic acid and heated in a first reaction zone at a temperature of 500°F. at atmospheric pressure for 3 hours. Water vapor and gaseous toluene are removed as fast as produced. The resultant isophthalic acid product is dissolved in a molar excess of molten toluic acid in a second reaction zone and maintained at a temperature of 480°F. for 1 hour. Any additional gaseous toluene is removed and the solution is then cooled to 300°F. to crystallize out the isophthalic acid which is removed by filtration. The isophthalic acid filter cake is slurried with hot xylene and filtered. The isophthalic acid so purified has a nitrogen content, determined as ammonia, of 0.16% and a neutralization equivalent of 82.5 (theoretical 83.1). The toluene product may be hydrolyzed to toluic acid and recycled to the first reaction zone with a fresh charge of the nitrogen-containing isophthalic acid.

Example 2

Terephthalic acid is produced pursuant to the invention in the following manner. 1 molar part of a mixture of diammonium terephthalate, diamid of terephthalic acid and the half-salt half-amide of terephthalic acid containing 6 to 10% by weight of nitrogen is mixed with 3 molar parts of benzoic acid and heated in a first reaction zone at a temperature of 500°F. at atmospheric pressure for 2 hours. Water vapor and gaseous benzonitrile are removed as formed. The resultant terephthalic acid product suspended in excess of molten benzoic acid is maintained at a temperature of 480°F.
3 for 1 hour in a second reaction zone. Any additional gaseous benzonitrile is removed and the solution is then cooled to 300° F. to crystallize out the terephthalic acid which is removed by filtration. Traces of benzoic acid are removed by sublimation from the terephthalic acid product by heating at 300° F. The terephthalic acid so purified has a nitrogen content, determined as ammonia, of 0.01% and a neutralization equivalent of 83.8 (theoretical 83.1). The benzonitrile product may be hydrolyzed to benzoic acid and recycled to the first reaction zone with a fresh charge of the nitrogen-containing phthalic acid.

It has also been observed that the reaction under the conditions described in the preceding examples is effectively catalyzed and the time for reaction decreased by the presence of inorganic acid materials such as sodium hydrogen sulfate, sulfuric acid or ammonium sulfate in amounts of .5 to 1% by weight.

In a further embodiment of the invention poly-substituted benzoic acid having all of its substituents selected from the group consisting of —COOH, —CONH₂ and —COONH₄ and having at least one nitrogen-containing substituent is hydrolyzed to produce benzene polycarboxylic acids of low nitrogen content by acidifying an aqueous solution of the mixture with a mineral acid to a pH in the range from about 2.5 to about 3.5 (this pH range is attained by adding approximately 1 equivalent of sulfuric acid to the solution of the mixture for each equivalent of ammonium carboxylate contained in the mixture), heating the mixture so acidified to a temperature above 300° F. and desirably in the range from 400° F. to 350° F., and preferably in the range from 430° F. to 500° F., under a superatmospheric pressure sufficient to maintain a substantial part of the water in liquid phase for a period of about 10 to 60 minutes and then cooling the mixture to a temperature below about 250° F., and filtering the cooled mixture to recover a filter cake consisting essentially of benzene polycarboxylic acids. It is desirable to reacidify the cooled mixture to pH 3 to 3.5 with a strong mineral acid prior to filtration. A single-stage treatment in this manner serves to reduce the nitrogen content of the benzene polycarboxylic acid product, determined as ammonia, from an initial value ordinarily in the range from 6 to 17% to a value in the range from about 0.6% to 1%.

The dried hydrolysis product is then mixed with a molar excess of benzoic or tolunitic acid and heated at a temperature of 400 to 600° F. at atmospheric pressure to produce the desired benzene polycarboxylic acid and benzoic or tolunitic which is continuously removed as a vapor. The residuall amide and ammonium salt groups react with the benzoic or tolunitic acid and quantitative removal of the residual nitrogen as benzonitrile or tolunitril is accomplished. When the reaction has been completed by continuous removal of the nitrile product, the benzene polycarboxylic acid is separated from solution in the excess of molten benzoic or tolunitic acid by cooling the solution to crystallize out the benzene polycarboxylic acid which is removed by filtration.

The present invention may be clearly understood by reference to the accompanying drawing. A meta-xylene feed is introduced through line 1 into the oxidation zone 2 where it is heated with ammonium sulfate, a sulfide such as H₂S, ammonium sulfide or ammonium polysulfide and water to a temperature of about 620° F. under a pressure of 2880 p. s. i. g. for 2 hours, according to the method of copending application Serial No. 377,209 as described above. The resultant mixture of dimmonium isophthalate, diamide of isophthalic acid, and the half-salt half-amide of isophthalic acid containing 6 to 17% nitrogen is then carbon treated and filtered in zone 3 and the mixture transferred through line 5 to the hydrolysis zone 6. Unreacted products from the oxidation process are removed through line 4 for purification prior to being recycled to oxidation zone 3. In the hydrolysis zone 6 an aqueous solution of the ammonium salt and amide mixture is mixed with sufficient mineral acid to produce a pH in the range of about 2.5 to 3.5. The acidic mixture is heated to a temperature in the range from 430° F. to 500° F., under a superatmospheric pressure sufficient to maintain a substantial part of the water in liquid phase for a period of about 10 to 60 minutes, in accordance with the single-stage hydrolysis method described above. The product is then removed through line 7, cooled to a temperature below about 250° F., readjusted to pH 3, filtered and dried in zone 8 to recover a product consisting essentially of isophthalic acid. A single-stage treatment in this manner serves to reduce the nitrogen content of the isophthalic acid product, determined as ammonia, from an initial value in the range from 6 to 17% to a value in the range from about .6 to 1%.

The isophthalic acid containing about 1% or less of nitrogen is then transferred to reaction zone 9 where it is mixed with a molar excess of molten benzoic acid and meta-toluic acids and heated at a temperature of 500° F. at atmospheric pressure for 3 hours. Water vapor and gaseous benzonitrile are removed as formed through line 10 and transferred to hydrolysis zone 11 for conversion of the benzonitrile to benzoic acid which is returned to reaction zone 9. Ammonia (as (NH₄)₂SO₄), resulting from hydrolysis of the nitrate group to the carboxyl group, is recycled to the xylene oxidation zone through line 12. If desired, the hydrolysis of the nitrate can be carried out in hydrolysis zone 6 with return of ammonia to oxidation zone 2 and acidification of the hydrolysis product effluent from zone 6 to precipitate a mixture of the monocarboxylic acid and partially purified phthalic acid which is charged to reaction zone 9. Alternatively, the benzonitrile can be recycled to oxidation zone 2 for conversion to a mixture of the amide and ammonium salt with subsequent conversion to benzoic acid in the hydrolysis zone 6.

The isophthalic acid reaction product dissolved in the molten excess of benzoic acid is removed through line 13 to a separation zone 14 where the solution is cooled to 300° F. to crystallize out the isophthalic acid which is removed by filtration. The molten benzoic filtrate is recycled through line 15 to reaction zone 9. If desired, a portion of the benzoic acid can be recycled to the oxidation zone 2 through line 16 for oxidation of impurities and/or a portion can be bleched by line 17 for purification from contaminants before it is recycled to the system. The isophthalic acid product is then removed through line 18 to a purification zone 19 where it is washed with hot xylene, hot water, or both, to remove traces of benzoic acid.

Example 3

Isophthalic acid is prepared pursuant to the invention by mixing and heating an isophthalic acid mixture containing the dried acid and the amide, which has been produced from meta-xylene according to the oxidation method described above, and thereafter reduced to about 1% nitrogen content according to the single-stage hydrolysis method described above, with a molar excess of benzoic acid at a temperature of 500° F. at atmospheric pressure for two hours. Benzonitrile and water vapor are removed continuously to effect a quantitative removal of nitrogen contained in the phthalic acid. The product solution is cooled to 300° F. to crystallize out the isophthalic acid which is then separated from the benzoic acid by filtration. The phthalic acid filter cake is washed twice with hot xylene and once with hot water. The isophthalic acid so purified has a nitrogen content determined as ammonia of .005% by weight and a neutralization equivalent of 83.0 (theoretical 83.1%).

Example 4

Isophthalic acid is prepared pursuant to the invention in the following manner. 50 pounds of a dry isophthalic acid is fed through line 1 into the oxidation zone 2 where it is heated with ammonium sulfate, a sulfide such as H₂S, ammonium sulfide or ammonium polysulfide and water to a temperature of about 620° F. under a pressure of 2880 p. s. i. g. for 2 hours, according to the method of copending application Serial No. 377,209 as described above. The resultant mixture of dimmonium isophthalate, diamide of isophthalic acid, and the half-salt half-amide of isophthalic acid containing 6 to 17% nitrogen is then carbon treated and filtered in zone 3 and the mixture transferred through line 5 to the hydrolysis zone 6. Unreacted products from the oxidation process are removed through line 4 for purification prior to being recycled to oxidation zone 3. In the hydrolysis zone 6 an aqueous solution of the ammonium salt and amide mixture is mixed with sufficient mineral acid to produce a pH in the range of about 2.5 to 3.5. The acidic mixture is heated to a temperature in the range from 430° F. to 500° F., under a superatmospheric pressure sufficient to maintain a substantial part of the water in liquid phase for a period of about 10 to 60 minutes, in accordance with the single-stage hydrolysis method described above. The product is then removed through line 7, cooled to a temperature below about 250° F., readjusted to pH 3, filtered and dried in zone 8 to recover a product consisting essentially of isophthalic acid. A single-stage treatment in this manner serves to reduce the nitrogen content of the isophthalic acid product, determined as ammonia, from an initial value in the range from 6 to 17% to a value in the range from about .6 to 1%.

The isophthalic acid containing about 1% or less of nitrogen is then transferred to reaction zone 9 where it is mixed with a molar excess of molten benzoic acid and meta-toluic acids and heated at a temperature of 500° F. at atmospheric pressure for 3 hours. Water vapor and gaseous benzonitrile are removed as formed through line 10 and transferred to hydrolysis zone 11 for conversion of the benzonitrile to benzoic acid which is returned to reaction zone 9. Ammonia (as (NH₄)₂SO₄), resulting from hydrolysis of the nitrate group to the carboxyl group, is recycled to the xylene oxidation zone through line 12. If desired, the hydrolysis of the nitrate can be carried out in hydrolysis zone 6 with return of ammonia to oxidation zone 2 and acidification of the hydrolysis product effluent from zone 6 to precipitate a mixture of the monocarboxylic acid and partially purified phthalic acid which is charged to reaction zone 9. Alternatively, the benzonitrile can be recycled to oxidation zone 2 for conversion to a mixture of the amide and ammonium salt with subsequent conversion to benzoic acid in the hydrolysis zone 6.

The isophthalic acid reaction product dissolved in the molten excess of benzoic acid is removed through line 13 to a separation zone 14 where the solution is cooled to 300° F. to crystallize out the isophthalic acid which is removed by filtration. The molten benzoic filtrate is recycled through line 15 to reaction zone 9. If desired, a portion of the benzoic acid can be recycled to the oxidation zone 2 through line 16 for oxidation of impurities and/or a portion can be bleched by line 17 for purification from contaminants before it is recycled to the system. The isophthalic acid product is then removed through line 18 to a purification zone 19 where it is washed with hot xylene, hot water, or both, to remove traces of benzoic acid.
acid mixture, prepared from the oxidation of meta-xylene, according to the oxidation method described above, and thereafter reduced to about 1% nitrogen content according to the single-stage hydrolysis method described above, and 250 pounds of benzoic acid are charged to a 310 steel 50 gallon kettle equipped with a column, condenser and reclaimer. The kettle contents are heated to 495° F. for 2 hours, 60 pounds of benzonitrile and benzoic acid condensate being taken overhead during this period. The kettle contents are cooled to 270° F., 15 gallons of xylene added and the temperature adjusted to 250° F. The kettle content are filtered and washed with 15 gallons of hot xylene at 250° F. The isophthalic acid filter cake is recharged to the kettle with 30 gallons of xylene and heated at 250° F. for one hour, filtered and washed with 15 gallons of xylene. The cake is again recharged with 30 gallons of water and heated at 180° F. for two hours. The batch is filtered, washed with hot water (30 gallons) and dried in a vacuum oven to give 36 pounds of isophthalic acid. The remainder of the isophthalic acid is taken as samples or left in the xylene and aqueous solutions. The isophthalic acid so prepared shows the following analysis:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hazen color of 20% aqueous solution of its sodium salt</td>
<td>100.0</td>
</tr>
<tr>
<td>Nitrogen as Ammonia, wt. percent</td>
<td>≤0.015</td>
</tr>
<tr>
<td>Sulfur, wt. percent</td>
<td>≤0.003</td>
</tr>
<tr>
<td>Benzoic acid, wt. percent</td>
<td>≤0.01 %</td>
</tr>
<tr>
<td>Appearance</td>
<td>White, free-flowing</td>
</tr>
</tbody>
</table>

Seive analysis, wt. percent:

- 100 mesh: 58%
- 200 mesh: 25%
- 325 mesh: 6%
- 325 mesh: 10%

While the foregoing examples illustrate the process of the invention using benzoic and toullic acids, the poly-substituted benzene feeds may be similarly converted to benzene polycarboxylic acids by heating with other aromatic monocarboxylic acids, such as nuclear substituted benzoic acids, in which the nuclear substituents are lower alkyl groups, halogen atoms, and the like, naphthoic acid and substituted naphthoic acids.

The phthalic acid amide-ammonium salt mixtures purified pursuant to the invention may in some instances contain a minor proportion of nitrile which is effectively and completely converted by the process of the invention.

I claim:

1. A process for producing essentially nitrogen-free phthalic acids which comprises heating di-substituted benzene having both of its substituents selected from the group consisting of —COOH, —CONH₂ and —COONH₄ and having at least one nitrogen-containing substituent with a molar excess of an acid selected from the group consisting of benzoic acid and tollic acid.

2. A process for producing essentially nitrogen-free phthalic acids which comprises hydrolyzing di-substituted benzene having both of its substituents selected from the group consisting of —COOH, —CONH₂ and —COONH₄ and having at least one nitrogen-containing substituent and removing residual nitrogen from the hydrolysate product by heating it with a molar excess of an acid selected from the group consisting of benzoic acid and tollic acid, cooling and separating the phthalic acid by fractional crystallization and filtration.

3. A process for producing essentially nitrogen-free benzene polycarboxylic acids which comprises forming a solution of a poly-substituted benzene, having essentially all of its substituents other than hydrogen selected from the group consisting of —COOH, —CONH₂ and —COONH₄ and having at least one nitrogen-containing substituent, in a molar excess of an aromatic monocarboxylic acid, heating the solution to 400 to 600° F., and cooling the solution to crystallize the benzene polycarboxylic acid therefrom.

4. A process for producing substantially pure isophthalic acid and terephthalic acid from the crude phthalic acid containing associated impurities resulting from the oxidative preparation thereof which comprises heating the phthalic acid with a molar excess of an aromatic monocarboxylic acid to 400 to 600° for 0.1 hour to 4.0 hours and cooling the solution to crystallize the phthalic acid therefrom.

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