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(54) Title: LIQUID PHASE OXIDATION OF HALOGENATED ORTHO-XYLENES

(57) Abstract: A method for the manufacture of halophthalic acid by liquid phase oxidation of haloortho-xylene is disclosed. The halophthalic acid may be dehydrated to form halophthalic anhydride which is useful in the synthesis of polyetherimide.



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LIQUID PHASE OXIDATION OF HALOGENATED ORTHO-XYLENES

BACKGROUND OF INVENTION

This invention relates to liquid phase oxidation of halogen substituted alkyl aromatic compounds. In particular, the invention relates to liquid phase oxidation of halo-ortho-xylene to produce halophthalic acid which can be dehydrated to produce halophthalic anhydride.

Liquid phase oxidation has long been used to produce dicarboxylic acids from dialkyl benzenes. Of particular interest has been the oxidation of dimethyl benzene (xylene) to phthalic acid, especially the oxidation of para-xylene to terephthalic acid, which is used in the production of polybutylene terephthalate. The liquid phase oxidation of xylene to phthalic acid requires the use of a catalyst, typically a cobalt/manganese/bromine catalyst system, and is generally performed in a carboxylic acid solvent such as acetic acid. The catalyst system may be augmented by the use of a co-catalyst such as zirconium, hafnium or cerium. Phthalic acid is an easily isolable solid, which can be filtered out of the reaction mixture.

Liquid phase oxidation, using a cobalt/manganese/bromine catalyst system and a carboxylic acid solvent, has also been applied to halogenated xylene with some success. The oxidation of the halogenated xylene is more difficult than the oxidation of xylene due to presence of a halogen, which is an electron withdrawing substituent, on the benzene ring. The greater difficulty in oxidation results in a lower reaction selectivity and a larger amount of partial oxidation and side products than seen in the liquid phase oxidation of xylene under similar conditions. Additionally, halogenated phthalic acid is difficult to separate from the partial oxidation and side products, even by distillation. Thus it is clear that in order for a method of liquid phase oxidation of halogenated xylene to be commercially successful the reaction yield and the reaction selectivity must be very high. Optimally, for a useful commercial process, the reaction selectivity should be high enough to result in only negligible amounts of partial oxidation and side products thus removing the need for isolation of halophthalic acid.

SUMMARY OF INVENTION

A method for the manufacture of halophthalic acid comprises forming a reaction mixture comprising a mixture of about 7 to about 3 parts by weight of acetic acid to 1 part by weight of a halo-ortho-xylene, about 0.25 to about 2 mole percent, based on the halo-ortho-xylene, of a cobalt source, about 0.1 to about 1 mole percent, based on the halo-ortho-xylene, of a manganese source, about 0.01 to about 0.1 mole percent, based on the halo-ortho-xylene, of a source of a metal selected from zirconium, hafnium and mixtures thereof, and about 0.02 to about 0.1 mole percent, based on the halo-ortho-xylene, of a bromide source; maintaining the reaction mixture at a pressure of at least about 1600 kilopascals (Kpa) and at a temperature of about 130°C to about 200°C; introducing a molecular oxygen containing gas to the reaction mixture at a rate of at least about 0.5 normal m³ of gas/hour per kilogram (kg) of halo-ortho-xylene in the reaction mixture for a time sufficient to provide at least about 90 percent conversion of the halo-ortho-xylene to halophthalic acid.

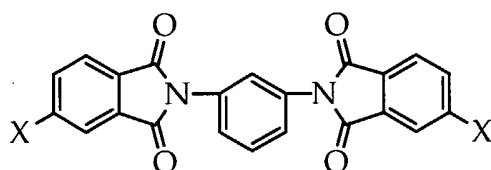
In another embodiment, a method for the manufacture of halophthalic anhydride comprises forming a reaction mixture comprising a mixture of about 7 to about 3 parts by weight of acetic acid to 1 part by weight of a halo-ortho-xylene, about 0.25 to about 2 mole percent, based on said halo-ortho-xylene, of a cobalt source, about 0.1 to about 1 mole percent, based on said halo-ortho-xylene, of a manganese source, about 0.01 to about 0.1 mole percent, based on said halo-ortho-xylene, of a source of a metal selected from zirconium, hafnium and mixtures thereof, and about 0.02 to about 0.1 mole percent, based on said halo-ortho-xylene, of a bromide source; maintaining said reaction mixture at a pressure of at least about 1600 Kpa and at a temperature of about 130°C to about 200°C; introducing a molecular oxygen containing gas to the reaction mixture at a rate of at least about 0.5 normal m³ of gas/kg of halo-ortho-xylene for a time sufficient to provide at least about 90 percent conversion of said halo-ortho-xylene to halophthalic acid with less than about 600 parts per million (ppm) of halophthalide; removing the acetic acid and any water formed as a result of the reaction by distillation; and dehydrating the halophthalic acid to form halophthalic anhydride.

In another aspect, the method for the manufacture of halophthalic acid comprises forming a reaction mixture comprising a mixture of about 7 to about 3 parts by weight of acetic acid to 1 part by weight of a halo-ortho-xylene, about 0.8 to about 1.2 mole percent, based on the halo-ortho-xylene, of a cobalt source, about 0.4 to about 0.6 mole percent, based on the halo-ortho-xylene, of a manganese source, about 0.04 to about 0.06 mole percent, based on the halo-ortho-xylene, of a source of a metal selected from zirconium, hafnium and mixtures thereof, and less than about 0.04 mole percent, based on the halo-ortho-xylene, of a source of bromide; maintaining the reaction mixture at a pressure of at least about 1600 Kpa and at a temperature of about 130°C to about 200°C; introducing a molecular oxygen containing gas to the reaction mixture at a rate of at least about 0.5 normal m³ of gas/kg of halo-ortho-xylene for a time sufficient to provide at least about 90 percent conversion of said halo-ortho-xylene to halophthalic acid.

In another aspect, a method for the manufacture of halophthalic anhydride comprises forming a reaction mixture comprising a mixture of about 7 to about 3 parts by weight of acetic acid to 1 part by weight of a halo-ortho-xylene, about 0.8 to about 1.2 mole percent, based on said halo-ortho-xylene, of cobalt acetate or cobalt acetate hydrate, about 0.4 to about 0.6 mole percent, based on said halo-ortho-xylene, of manganese acetate or manganese acetate hydrate, about 0.04 to about 0.06 mole percent, based on said halo-ortho-xylene, of zirconium acetate or zirconium acetate hydrate, less than about 0.04 mole percent, based on said halo-ortho-xylene, of sodium bromide; maintaining said reaction mixture at a pressure of at least about 1600 Kpa and at a temperature of about 130°C to about 200°C; introducing a molecular oxygen containing gas to said reaction mixture at a rate of at least about 0.5 normal m³ of gas/kg of halo-ortho-xylene in the reaction mixture for a time sufficient to provide at least about 90 percent conversion of said halo-ortho-xylene to halophthalic acid; removing the acetic acid and any water formed as a result of the reaction by distillation; separating the water from the acetic acid and recycling the acetic acid; and dehydrating the halophthalic acid to form halophthalic anhydride.

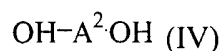
In another embodiment, a method for the manufacture of polyetherimide comprises forming a reaction mixture comprising a mixture of about 7 to about 3 parts by weight

of acetic acid to 1 part by weight of a halo-ortho-xylene, about 0.25 to about 2 mole percent, based on the halo-ortho-xylene, of a cobalt source, about 0.1 to about 1 mole percent, based on the halo-ortho-xylene, of a manganese source, about 0.01 to about 0.1 mole percent, based on the halo-ortho-xylene, of a source of a metal selected from zirconium, hafnium and mixtures thereof, about 0.02 to about 0.1 mole percent, based on the halo-ortho-xylene, of a bromide source; maintaining the reaction mixture at a pressure of at least about 1600 KPa and at a temperature of about 130°C to about 200°C; introducing a molecular oxygen containing gas to the reaction mixture at a rate of at least about 0.5 normal m³ of gas/kg of halo-ortho-xylene for a time sufficient to provide at least about 90 percent conversion of the halo-ortho-xylene to halophthalic acid with less than about 600 parts per million (ppm) of halophthalide; removing the acetic acid and any water formed as a result of the reaction by distillation; dehydrating the halophthalic acid to form halophthalic anhydride; reacting the halophthalic anhydride with 1,3-diaminobenzene to form bis(halophthalimide) (II)



(II)

wherein X is a halogen; and reacting bis(halophthalimide) (II) with an alkali metal salt of a dihydroxy substituted aromatic hydrocarbon having the formula (IV)



wherein A² is a divalent aromatic hydrocarbon radical to form the polyetherimide.

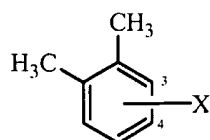
DETAILED DESCRIPTION

A method for the manufacture of halophthalic acid comprises forming a reaction mixture comprising a mixture of about 7 to about 3 parts by weight of acetic acid to 1 part by weight of a halo-ortho-xylene, about 0.25 to about 2 mole percent, based on the halo-ortho-xylene, of a cobalt source, about 0.1 to about 1 mole percent, based on

the halo-ortho-xylene, of a manganese source, about 0.01 to about 0.1 mole percent, based on the halo-ortho-xylene, of a source of a metal selected from zirconium, hafnium and mixtures thereof, and about 0.02 to about 0.1 mole percent, based on the halo-ortho-xylene, of a bromide source. The reaction mixture is maintained at a pressure of at least about 1600 Kpa and at a temperature of about 130°C to about 200°C. A molecular oxygen containing gas is introduced to the reaction mixture at a rate of at least about 0.5 normal m³ of oxygen containing gas /hour per kg of halo-ortho-xylene in the reaction mixture for a time sufficient to provide at least about 90 percent conversion of the halo-ortho-xylene to halophthalic acid. The introduction of the molecular oxygen containing gas creates an oxygen containing off gas, which preferably has an oxygen concentration of less than about 3 percent by volume of the off gas.

Using the method for manufacture of halophthalic acid and anhydride described herein, the high yield synthesis of high purity halophthalic acid and anhydride is possible on a scale employing hundreds of kilograms of halo-ortho-xylene by liquid phase oxidation in the presence of about 0.25 to about 2 mole percent (mol%) of a cobalt source, about 0.1 to about 1 mol% of a manganese source, about 0.01 to about 0.1 mol% of a source of a metal selected from zirconium, hafnium and mixtures thereof, and about 0.02 to about 0.1 mol% of a bromide source. Applicants have discovered that in large scale liquid phase oxidations employing halo-ortho-xylene the amount of bromide can have a significant impact on the amount of impurities present in the final product. The use of decreasing molar percentages of bromide result in a product, either halophthalic acid or anhydride, with a decreased level of impurities such as halophthalide. While the reasons for this phenomenon are not clearly understood it is contemplated that even lower levels of bromide, molar percentages less than about 0.02, may be useful in producing high purity halophthalic acid or anhydride in even larger scale liquid phase oxidations such as those employing thousands of kilograms of halo-ortho-xylene.

Halo-ortho-xylene suitable for use in the oxidation has the structure (IV)



(IV)

wherein X is halogen. Preferably X is chlorine. The halogen substituent may be in the 3 position (the 3-isomer) or in the 4 position (the 4-isomer). The halo-ortho-xylene used in the liquid-phase oxidation may also be a mixture of the 3-isomer and the 4-isomer.

The liquid phase oxidation preferably employs acetic acid as a solvent although other lower carboxylic acids may be employed, as readily appreciated by one of ordinary skill in the art. In general, acetic acid with a water content of up to about 3 percent may be employed. Typically the acetic acid is present in an amount of 7 to 3 parts by weight to 1 part by weight of halo-ortho-xylene. Preferably the acetic acid is present in an amount of 5 to 3 parts by weight to 1 part by weight of halo-ortho-xylene.

Suitable molecular oxygen containing gases include gases or combinations of gases which are a source of molecular oxygen (O₂), for example, 100% oxygen and mixtures of oxygen with inert gas with a sufficient concentration of oxygen to effect oxidation. Sufficient oxygen concentrations typically are greater than or equal to about 6% oxygen, preferably greater than or equal to about 15%, more preferably greater than or equal to about 20%. Clearly mixtures with greater than or equal to about 50% oxygen may also be used. As will be appreciated by one of skill in the art, the concentration of oxygen may affect the rate of the reaction. A preferred molecular oxygen containing gas is air.

Useful cobalt, manganese, bromine, zirconium, and hafnium sources are those sources which are soluble in acetic acid. As to the cobalt, manganese, zirconium or hafnium sources these include the metals themselves or any of their salts, complexes or compounds. These include, but are not limited to, acetates, citrates, stearates, naphthenates, acetylacetonates, benzoylacetonates, carbonates, sulfates, bromides, chlorides, fluorides, nitrates, hydroxides, alkoxides, nitrides, triflates, hydrates of the

foregoing and mixtures of the foregoing. Preferably the cobalt in the cobalt source is in a +2 or +3 oxidation state. Preferably the manganese in the manganese source is in a +2 or +3 oxidation state. Examples of bromide sources include, but are not limited to, bromine, hydrogen bromide, a metal-bromide salt such as sodium bromide and organic bromides. Examples of organic bromides include tetrabromoethane, ethyl bromide, ethylene bromide, bromoform, xylyl bromide, xylylene bromide and mixtures comprising at least one of the organic bromides.

The mole percent (mol%) of the cobalt, manganese, zirconium, hafnium, and bromine are based on the amount of halo-ortho-xylene present at the beginning of the reaction. The cobalt source is generally present in amounts of about 0.25 to about 2 mol%. Preferably, the cobalt source is present in an amount of less than about 1.2 mol%. In addition, it is also preferable for the cobalt source to be present in an amount greater than or equal to about 0.5 mol%, and more preferably in an amount greater than or equal to about 0.8 mol%. It is particularly preferred for the amount of the cobalt source to be about 1 mol%.

The manganese source is present in amounts of about 0.1 to about 1 mol%. Preferably, the manganese source is present in an amount of less than or equal to about 0.6 mol%. Additionally, it is also preferable for the manganese source to be present in an amount greater than or equal to about 0.3 mol%, more preferably greater than or equal to about 0.4 mol%. In a particularly preferred embodiment, the manganese source is present in an amount of about 0.5 mol%.

The bromide source is generally present in amounts of about 0.02 to about 0.1 mol%. Preferably, the amount of the bromide source is less than or equal to 0.8 mol%, more preferably less than or equal to about 0.5 mol%, even more preferably less than or equal to 0.4 mol%, and most preferably less than or equal to 0.3 mol%.

The zirconium source, hafnium source or mixture thereof is generally present in amounts of about 0.01 to about 0.1 mol%. Preferably, the zirconium source, hafnium source or mixture thereof is present in an amount less than or equal to about 0.06 mol%. Additionally it is also preferable for, the zirconium source, hafnium source or mixture thereof to be present in an amount greater than or equal to about 0.03 mol%,

more preferably greater than 0.04 mol%. In a particularly preferred embodiment, the zirconium source, hafnium source or mixture thereof is present in an amount of about 0.05 mol%.

In an exemplary process, the halophthalic acid may be produced by combining halo-ortho-xylene; the cobalt source; the manganese source; the bromine source; and the zirconium source, hafnium source or mixture thereof, in acetic acid in a reaction vessel. The reaction vessel is established at a pressure of greater than about 1600 Kpa at the desired temperature. The temperature of the reaction is typically about 130°C to about 200°C, preferably about 150°C to about 170°C, and more preferably greater than about 160°C. The molecular oxygen containing gas is then introduced. The flow of the molecular oxygen containing gas creates an oxygen containing off gas that preferably has an oxygen concentration of less than 3% by volume, preferably less than about 1% by volume. The oxygen concentration of the off gas may be determined by paramagnetic transduction oxygen analysis or other method known in the art. Useful flow rates are typically greater than or equal to 0.5 normal cubic meter (m³)/hour per kilogram (kg) of halo-ortho-xylene and preferably greater than or equal to 1.0 normal cubic meter (m³)/hour per kilogram (kg) of halo-ortho-xylene. A normal cubic meter is defined as cubic meter under standard temperature and pressure condition. Preferably the reaction mixture is agitated using standard methods such as mechanical stirring. The flow of molecular oxygen containing gas is continued until at least about 90% of halo-ortho-xylene has been converted to halophthalic acid, preferably until greater than 95% has been converted. The amount of conversion achieved in the reaction can readily be determined through the use of gas chromatography, mass spectrometry or other methods known in the art. In our experience, amount of time required to reach 90% conversion of halo-ortho-xylene is about 3 to about 6 hours.

Additionally, the method to manufacture halophthalic acid or anhydride may include the optional step of monitoring the oxygen concentration of the off gas. When the oxygen concentration of the off gas exceeds about 3% by volume that signals a slowing of the reaction. Once the oxygen concentration of the off gas exceeds about 3% by volume the flow of the molecular oxygen containing gas may be modified so as

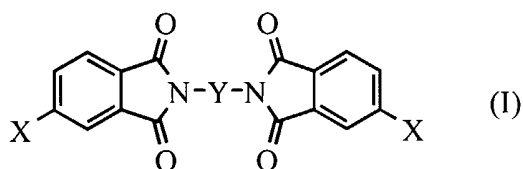
to maintain the oxygen concentration of the off gas below about 5% by volume. The flow of the molecular oxygen containing gas may be modified in several ways. The molecular oxygen containing gas may be diluted with an inert gas so as to decrease the oxygen concentration in the molecular oxygen containing gas, the flow rate of the molecular oxygen containing gas may be decreased, the source of the molecular oxygen containing gas may be changed so as to employ a molecular oxygen containing gas with a lower oxygen concentration or these methods may be combined so as to maintain the oxygen concentration of the off gas below about 5% by volume. The modified flow of molecular oxygen containing gas may then be continued until at least about 90% of halo-ortho-xylene has been converted to halophthalic acid, preferably until greater than 95% has been converted. The amount of conversion achieved in the reaction can readily be determined through the use of gas chromatography, mass spectrometry or other methods known in the art.

After the reaction reaches the desired level of completion, the halophthalic acid may be recovered as halophthalic acid or halophthalic anhydride. Many applications such as pharmaceutical applications and polymer synthesis require halophthalic acid and halophthalic anhydride with a high degree of purity. Such high degree of purity may be achieved by the method described herein. In fact, halophthalic acid and halophthalic anhydride containing less than about 600 ppm of halophthalide, preferably less than about 500 ppm of halophthalide, and more preferably less than about 400 ppm of halophthalide is readily achievable. Additionally, chlorophthalic acid and chlorophthalic anhydride containing less than about 1% by weight of phthalic anhydride and chlorobenzoic acid may also be achieved. Chlorotoluic acids and dichlorophthalic acids are typically not detected.

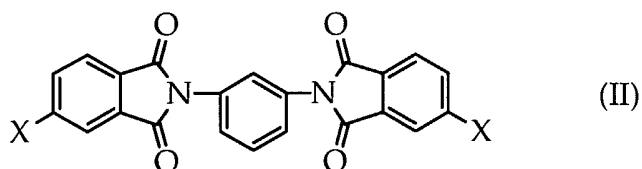
Most of the acetic acid as well as water produced in the reaction can be removed by distillation at approximately atmospheric pressure, typically by heating to about 200°C at 200 Kpa. The acetic acid and water are removed as a vapor and condensed. The water may then be removed from the acetic acid and the acetic acid may be recycled. Some dehydration of the halophthalic acid to form halophthalic anhydride may occur simultaneously with the removal of acetic acid and water. Furthermore, the removal of acetic acid and water may be combined with dehydration to form a single step.

Dehydration is typically done thermally by distillation under vacuum at an elevated temperature allowing dehydration and isolation of the halophthalic anhydride from any remaining acetic acid and water to occur simultaneously. Dehydration may also be carried out by other chemical reactions well known to those skilled in the art such as treatment with acetic anhydride. After distillation the halophthalic anhydride is typically greater than about 95 percent, preferably greater than about 97 percent, and most preferably greater than about 99 percent pure. Halophthalic anhydrides of high purity are used in the synthesis of polyetherimide, a high heat engineering plastic.

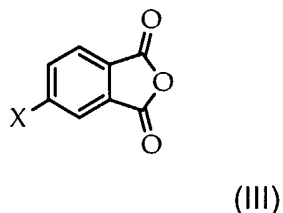
Polyetherimides are high heat engineering plastics having a variety of uses. One route for the synthesis of polyetherimides proceeds through a bis(4-halophthalimide) having the following structure (I):



wherein Y is a divalent alkylene, cycloalkylene, or arylene moiety and X is a halogen. The bis(4-halophthalimide) wherein Y is a 1,3-phenyl group (II) is particularly useful.

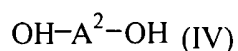


Bis(halophthalimide)s (I) and (II) are typically formed by the condensation of amines, e.g., 1,3-diaminobenzene with anhydrides, e.g., 4-halophthalic anhydride (III):



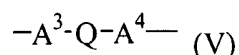
Polyetherimides may be synthesized by the reaction of the bis(halophthalimide) with an alkali metal salt of a dihydroxy substituted aromatic hydrocarbon in the presence or

absence of phase transfer catalyst. Suitable phase transfer catalysts are disclosed in U.S. Patent No. 5,229,482, which is herein incorporated by reference. Suitable dihydroxy substituted aromatic hydrocarbons include those having the formula (IV)



wherein A^2 is a divalent aromatic hydrocarbon radical. Suitable A^2 radicals include m-phenylene, p-phenylene, 4,4'-biphenylene, 4,4'-bi(3,5-dimethyl)phenylene, 2,3-bis(4-phenylene)propane and similar radicals such as those disclosed by name or formula in U.S. Patent No. 4,217,438.

The A^2 radical preferably has the formula (V)



wherein each of A^3 and A^4 is a monocyclic divalent aromatic hydrocarbon radical and Q is a bridging hydrocarbon radical in which one or two atoms separate A^3 from A^4 . The free valence bonds in formula (V) are usually in the meta or para positions of A^3 and A^4 in relation to Y. A^3 and A^4 may be substituted phenylene or hydrocarbon-substituted derivative thereof, illustrative substituents (one or more) being alkyl and alkenyl. Unsubstituted phenylene radicals are preferred. Both A^3 and A^4 are preferably p-phenylene, although both may be o- or m-phenylene or one o- or m-phenylene and the other p-phenylene.

The bridging radical, Q, is one in which one or two atoms, preferably one, separate A^3 from A^4 . Illustrative radicals of this type are methylene, cyclohexylmethylene, 2-(2,2,1)-bicycloheptylmethylene, ethylene, isopropylidene, neopentylidene, cyclohexylidene, and adamantylidene. The preferred radical of formula (IV) is 2,2-bis(4-phenylene)propane radical which is derived from bisphenol A and in which Q is isopropylidene and A^3 and A^4 are each p-phenylene.

It is clear to one of ordinary skill in the art that any impurities present in the halophthalic anhydride will be carried through to subsequent steps in the polyetherimide synthesis. The presence of significant levels of impurities in

subsequent steps can interfere with polymerization and cause discoloration of the final product, polyetherimide.

All patents cited are herein incorporated by reference.

The invention is further illustrated by the following non-limiting examples.

EXAMPLES 1-5

In a laboratory scale reactor 492 grams (g) (3.5 mol) of chloro-ortho-xylene (a mixture of about 30% 3-chloro-ortho-xylene and about 70% 4-chloro-ortho-xylene), 1925g of glacial acetic acid, 8.7g (1 mol%) of cobalt acetate tetrahydrate, 4.3g (0.5 mol%) of manganese acetate tetrahydrate, 1.0g (0.06 mol%) zirconium acetate solution, 4.3 g (1.5 mol%) sodium acetate and varying amounts of sodium bromide were combined. The reactor was filled with nitrogen, pressurized to 1900 KPa and heated to about 160°C. Air was then introduced to the reactor through a dip tube. Initially, the off gas oxygen concentration was greater than 0 but less than 1 percent. The reaction mixture was agitated throughout the reaction time. After about 3 hours the oxygen concentration of the off gas increased to greater than 3 percent. The flow of air was stopped. Air diluted with nitrogen so as to have an off gas oxygen concentration of about 5 percent was introduced to the reactor and the temperature of the reactor was increased to about 190°C. The flow of diluted air continued for about 1 to 3 hours. Chlorophthalic acid was determined to be present in an amount of 25 wt% based on the total weight of the reaction mixture. The majority of water formed by the reaction and the acetic acid were removed under atmospheric distillation. The chlorophthalic acid was dehydrated and any residual water and acetic acid were removed under heat and reduced pressure to form chlorophthalic anhydride. Chlorophthalic anhydride was separated from the catalyst by distillation under vacuum at distillation temperatures near 170°C. The isolated chlorophthalic acid was analyzed by gas chromatography. Results are shown in Table 1.

Table 1.

Example	NaBr mol%	Amount of Chlorophthalides produced

		wt%	ppm
1 *	1.0	0.57	5700
2 *	0.29	0.25	2500
3 *	0.14	0.01	100
4	0.03	0.46	4600
5 *	0.014	2.35	23500

* comparative examples

As can be seen by examples 1-5, chlorophthalic anhydride with very small amounts of chlorophthalide may be produced on a laboratory scale, however the amount of bromide required is greater than 0.05 mol%.

EXAMPLES 6-10

In a pilot scale reaction 200 kilograms (kg) of chloro-ortho-xylene (a mixture of 3-chloro-ortho-xylene and 4-chloro-ortho-xylene), 780 kg of acetic acid, 3.5 kg (1.0 mol %) cobalt acetate tetrahydrate, 1.75 kg (0.5 mol %) manganese acetate tetrahydrate, 0.4 kg (0.05 mol %) zirconium acetate solution, 1.75 kg (1.5 mol %) sodium acetate and varying amounts of sodium bromide were combined. The amount of sodium bromide was varied by example as shown in Table 2. The reactor was filled with nitrogen, pressurized to 1900 Kpa and heated to about 160°C. Air was introduced to the reactor through a dip tube at a flow rate gradually increasing to 200 normal m³/h. Initially, the off gas oxygen concentration was greater than 0 but less than 1 percent. The reaction mixture was agitated throughout the reaction time. After about 1 hour, the reaction temperature was increased to 175° C. After about 3 hours the off gas oxygen concentration increased to greater than 3 percent. The air flow was stopped. Air diluted with nitrogen so as to have an off gas oxygen concentration of about 5 percent was introduced into the reactor and the temperature of the reactor was increased to 190°C. The flow of diluted air was continued for about 3 hours. Final

weight of the reactor contents was consistent with high conversions of chloro-o-xylene based on the absorption of 3 moles of O_2 to generate the diacid and two moles of water. The majority of water formed by the reaction and the acetic acid were removed under atmospheric distillation. The chlorophthalic acid was dehydrated and any residual water and acetic acid were removed under heat and reduced pressure to form chlorophthalic anhydride. Chlorophthalic anhydride was separated from the catalyst by distillation under vacuum at distillation temperatures near $170^{\circ}C$. The isolated chlorophthalic acid was analyzed by gas chromatography. Results are shown in Table 2.

Table 2.

Example	NaBr mol %	Amount of Chlorophthalides produced	
		(wt%)	ppm
6*	1.02	5.4	54000
7*	0.14	0.24	2400
8*	0.10	0.12	1200
9	0.03	0.02	200
10	0.02	0.03	300

*comparative examples

As can be seen in the preceding examples it is possible to produce chlorophthalic anhydride with very low levels of chlorophthalide in reactions on a large scale. The overall purity of the chlorophthalic acid produced in Examples 9 and 10 was greater than 98%.

EXAMPLE 11

In a laboratory scale reactor 40 grams (g) (284 millimole (mmol)) of chloro-ortho-xylene (a mixture of about 30% 3-chloro-ortho-xylene and about 70% 4-chloro-ortho-xylene), 160g of glacial acetic acid, 567 milligrams (mg) (0.8 mol%) of cobalt acetate tetrahydrate, 349 mg (0.5 mol%) of manganese acetate tetrahydrate, 9.1 mg (0.06 mol%) zirconium acetate solution, and 91 mg of 30% solution by weight of hydrogen bromide in acetic acid were combined. The reactor was filled with nitrogen, pressurized to 1900 KPa and heated to about 160°C. Air was then introduced to the reactor through a dip tube. Initially, the off gas oxygen concentration was greater than 0 but less than 1 percent. The reaction mixture was agitated throughout the reaction time. After 1 hour at 160°C the temperature was increased to about 175°C. After

about 3 hours the oxygen concentration of the off gas increased to greater than 3 percent. The flow of air was stopped. Air diluted with nitrogen so as to have an off gas oxygen concentration of about 5 percent was introduced to the reactor and the temperature of the reactor was increased to about 190°C. The flow of diluted air continued for about 1 to 3 hours. The reaction mixture was analyzed by liquid chromatography (LC) and it was found that the chlorophthalic acid was formed with yield and impurity levels comparable to the results of Example 2.

Using the method for manufacture of halophthalic acid and anhydride described herein, the high yield synthesis of high purity halophthalic acid and anhydride is possible on a large scale employing hundreds of kilograms of halo-ortho-xylene by liquid phase oxidation in the presence of about 0.25 to about 2 mol% of a cobalt source, about 0.1 to about 1 mol% of a manganese source, about 0.01 to about 0.1 mol% of a source of a metal selected from zirconium, hafnium and mixtures thereof, and about 0.02 to about 0.1 mol% of a bromide source. Applicants have discovered that in large scale liquid phase oxidations employing halo-ortho-xylene the amount of bromide can have a significant impact on the amount of impurities present in the final product. The use of decreasing molar percentages of bromide result in either halophthalic acid or anhydride with a decreased level of impurities such as halophthalide. While the reasons for this phenomenon are not clearly understood it is contemplated that even lower levels of bromide, molar percentages less than about 0.02, may be useful in producing high purity halophthalic acid or anhydride in even larger scale liquid phase oxidations such as those employing thousands of kilograms of halo-ortho-xylene.

While the invention has been described with reference to a preferred embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this

invention, but that the invention will include all embodiments falling within the scope of the appended claims.

CLAIMS

WHAT IS CLAIMED IS:

1. A method for the manufacture of halophthalic acid comprising:

forming a reaction mixture comprising:

a mixture of about 7 to about 3 parts by weight of acetic acid to 1 part by weight of a halo-ortho-xylene,

about 0.25 to about 2 mole percent, based on said halo-ortho-xylene, of a cobalt source,

about 0.1 to about 1 mole percent, based on said halo-ortho-xylene, of a manganese source,

about 0.01 to about 0.1 mole percent, based on said halo-ortho-xylene, of a source of a metal selected from zirconium, hafnium and mixtures thereof,

about 0.02 to about 0.1 mole percent, based on said halo-ortho-xylene, of a source of bromide;

maintaining said reaction mixture at a pressure of at least about 1600 Kpa and at a temperature of about 130°C to about 200°C;

introducing a molecular oxygen containing gas to said reaction mixture at a rate of at least about 0.5 normal m³ of gas/kg of halo-ortho-xylene in said reaction mixture for a time sufficient to provide at least about 90 percent conversion of said halo-ortho-xylene to halophthalic acid.

2. The method of Claim 1 wherein introducing a molecular oxygen containing gas said reaction mixture creates an oxygen containing off gas and said oxygen containing off gas oxygen concentration is less than about one percent by volume of said off gas and further comprising maintaining said introduction of said molecular oxygen containing gas until the off gas oxygen concentration exceeds about 3 percent by volume of said off gas and modifying the introduction of said molecular oxygen

containing gas so as to maintain the off gas oxygen concentration at a concentration below about 5 percent by volume of said off gas and maintaining the modified introduction of said molecular oxygen containing gas for a time sufficient to provide at least about 90 percent conversion of said halo-ortho-xylene to halophthalic acid.

3. A method for the manufacture of halophthalic anhydride comprising forming a halophthalic acid by the method of Claims 1 or 2;

removing said acetic acid and any water formed as a result of the reaction by distillation; and

dehydrating said halophthalic acid to form halophthalic anhydride.

4. The method of any of the preceding claims wherein said halophthalic acid comprises less than 600 parts per million (ppm) of halophthalide

5. The method of any of the preceding claims, wherein the molecular oxygen containing gas has an oxygen concentration of greater than or equal to about 6% oxygen.

6. The method of any of the preceding claims, wherein the molecular oxygen containing gas is air.

7. The method of any of the preceding claims, wherein the cobalt source, manganese source, zirconium or hafnium source, and bromide source are soluble in acetic acid.

8. The method of Claim 7, wherein the cobalt source comprises cobalt acetate, cobalt napthenate, cobalt sulfate, cobalt acetylacetonate, cobalt benzoylacetonate, cobalt bromide, cobalt carbonate, cobalt chloride, cobalt fluoride, cobalt nitrate, cobalt stearate, or a hydrate of one of the foregoing cobalt compounds.

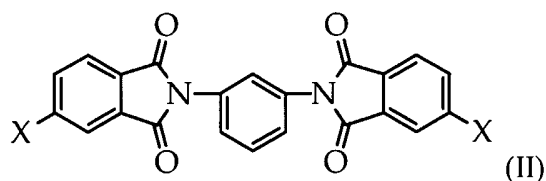
9. The method of Claim 7, wherein the manganese source comprises manganese acetate, manganese sulfate, manganese acetylacetonate, manganese bromide, manganese carbonate, manganese chloride, manganese fluoride, manganese nitrate, or a hydrate of one of the foregoing manganese compounds.

10. The method of Claim 7, wherein the zirconium source comprises zirconium acetate, zirconium sulfate, zirconium citrate, zirconium fluoride, zirconium hydroxide, zirconium alkoxide, zirconium chloride, zirconium bromide, zirconium acetylacetonate, or a hydrate of one of the foregoing zirconium compounds.
11. The method of Claim 7, wherein the source of hafnium comprises hafnium chloride, hafnium bromide, hafnium fluoride, hafnium iodide, hafnium nitride, hafnium sulfate, hafnium triflate, hafnium nitrate, or a hydrate of one of the foregoing hafnium compounds.
12. The method of Claim 7, wherein the bromide source comprises bromine, hydrogen bromide, a metal-bromide salt or an organic bromide.
13. The method of any of the preceding claims, wherein the amount of the cobalt source is about 0.5 to about 1.2 mole percent, the amount of the manganese source is about 0.3 to about 0.6 mole percent, the amount of the source of zirconium or hafnium is about 0.03 to about 0.06 mole percent, wherein the amount of the source of bromide is less than or equal to about 0.04 mole percent, based on said halo-ortho-xylene.
14. The method of any of the preceding claims, wherein the temperature is greater than or equal to 160°C.
15. The method of any of the preceding claims, wherein the conversion of said halo-ortho-xylene to halophthalic acid is 95 percent or greater.
16. The method of any of the preceding claims, wherein said halo-ortho-xylene comprises the 3-isomer, the 4-isomer or a mixture of 3- and 4-isomers.
17. The method of any of the preceding claims, wherein said acetic acid is recycled to the reaction mixture.
18. The method of any of the preceding claims wherein said halo-ortho-xylene is chloro-ortho-xylene.

19. The method of Claims 2-18, further comprising increasing the temperature of the reaction mixture while maintaining the off gas oxygen concentration below about 5 percent by volume.

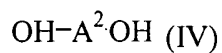
20. A method for the manufacture of polyetherimide comprising forming halophthalic anhydride by the method of Claims 3-19;

reacting said halophthalic anhydride with 1,3-diaminobenzene to form bis(halophthalimide) (II)



wherein X is a halogen; and

reacting bis(halophthalimide) (II) with an alkali metal salt of a dihydroxy substituted aromatic hydrocarbon having the formula (IV)



wherein A^2 is a divalent aromatic hydrocarbon radical to form the polyetherimide.

INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/US 03/07416

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C51/265 C07C51/56 C08G73/10

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 7 C07C

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 practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	NAZARENKO ET AL: "Preparation of monochlorophthalic acids by the liquid phase catalytic oxidation of chloro-o-xylenes" CHEMICAL ABSTRACTS + INDEXES, AMERICAN CHEMICAL SOCIETY. COLUMBUS, US, vol. 101, no. 25, 17 December 1984 (1984-12-17), XP002162265 ISSN: 0009-2258 abstract	1
A	UZULNIECE ET AL: "Liquid-phase catalytic oxidation of 4-bromo-o-xylene" CHEMICAL ABSTRACTS + INDEXES, AMERICAN CHEMICAL SOCIETY. COLUMBUS, US, vol. 90, no. 5, 1979, XP002165078 ISSN: 0009-2258 abstract	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

4 July 2003

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 112 992 A (BELMONTE FRANK G ET AL) 12 May 1992 (1992-05-12) the whole document -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/US 03/07416

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5112992	A	12-05-1992	NONE