

A PURIFICATION PROCESS OF CRUDE TEREPHTHALIC ACID IN A POST OXIDATION ZONE BY THE ADDITION OF STEAM

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FIELD OF INVENTION

The present invention relates to a process for heating carboxylic acid slurry in a post oxidation zone by the addition of steam. More specifically,
10 the present invention relates to a process for heating a terephthalic acid slurry in a post oxidation zone by the addition of steam in a process for the production of a crystallized product.

BACKGROUND OF THE INVENTION

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Terephthalic acid (TPA) is commercially produced by oxidation of paraxylene in the presence of a catalyst, such as, for example, Co, Mn, Br and a solvent. Terephthalic acid used in the production of polyester fibers, films, and resins must be further treated to remove impurities present due to
20 the initial oxidation of paraxylene. Typical commercial processes remove impurities by isolating a crude terephthalic acid solid, dissolving the solid in water at high temperatures and pressures, hydrogenating the resultant solution, cooling and crystallizing the terephthalic acid product out of solution, and separating the solid terephthalic product from the liquid as

discussed in U. S. Patent No. 3,584,039, herein incorporated by reference. Colored impurities from the benzil, anthraquinone, and fluorenone families are hydrogenated to colorless products and leave the process with the terephthalic acid solid product and wastewater streams.

5 Still other methods of obtaining a terephthalic acid product suitable as starting material for the production of polyesters do not involve a hydrogenation step. A method of producing a terephthalic acid product suitable for polyester production is to completely or nearly completely react paraxylene in a multiple stage oxidation process. In this invention, a unique
10 and novel process is provided wherein a crude terephthaic slurry produced by the oxidation of an aromatic feedstock, typically p-xylene, is further oxidized in a multiple step process wherein heat is provided to a post oxidation zone by steam addition. The addition of steam to an oxidation zone subsequent to the primary oxidation zone results in a higher quality
15 terephthalic acid product compared to conventional techniques.

SUMMARY OF THE INVENTION

 This invention provides a process to produce a crystallized product
20 from a crude carboxylic acid slurry by injecting steam in a post oxidation zone subsequent to the primary oxidation zone.

 In a first embodiment of this invention, a process to produce a post oxidation product is provided comprising

(a) oxidizing in a post oxidation zone a crude carboxylic acid slurry in the presence of steam to form the post oxidation product; wherein the post oxidation zone comprises at least one post oxidation device; wherein the crude carboxylic acid slurry comprises at least one carboxylic acid;

(b) purifying the post oxidation product to form a decolorized post oxidation product having b^* color of less than 4.5.

In another embodiment of this invention, a process to produce a crystallized product is provided. The process comprising the following steps:

(a) oxidizing in a post oxidation zone the crude carboxylic acid slurry in a post oxidation zone in the presence of steam to form a post oxidation product and an offgas stream; wherein the post oxidation zone comprises at least one post oxidation device;

(b) purifying the post oxidation product before or after the crystallization zone to form a decolorized post oxidation product having b^* color of less than 4.5; and

(c) crystallizing in a crystallization zone the post oxidation product; wherein the crystallization zone comprises at least one crystallizer.

In another embodiment of this invention, a process to produce a crystallized product is provided. The process comprises oxidizing in a post oxidation zone a crude carboxylic acid slurry in the presence of steam to form the post oxidation product; wherein the crude carboxylic acid slurry

comprises terephthalic acid; wherein the post oxidation zone comprises at least one post oxidation device; wherein the post oxidation product has a b* color of less than about 4.5.

In another embodiment of this invention, a process to produce a
5 crystallized product is provided. The process comprises the following steps:

(a) oxidizing the crude carboxylic acid slurry in a post oxidation zone in the presence of steam to form a post oxidation product; wherein the post oxidation zone comprises at least one post oxidation device; wherein
10 the pressure of the post oxidation zone is between about 10 barg to about 50 barg; and

(b) crystallizing in a crystallization zone the post oxidation product to form a crystallized product; wherein the crystallization zone comprises at least one crystallizer; wherein the crystallizer is operated at a temperature
15 between about 140°C and 190°C ; and wherein the crystallized product has a b* color of less than 4.5.

These objects, and other objects, will become more apparent to others with ordinary skill in the art after reading this disclosure.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic of a process for heating a crude carboxylic acid slurry in a post oxidation zone by the addition of steam to produce a post oxidation product.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process to produce a post oxidation product comprising oxidizing a crude carboxylic acid slurry in the presence of steam to form the post oxidation product **120** and a offgas stream **80**.

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In a first embodiment of this invention, a process to produce a post oxidation product **120** is provided. The process comprises oxidizing in a post oxidation zone **90** a crude carboxylic acid slurry **30** in the presence of steam **100** to form the post oxidation product **120** and an offgas stream **80**; wherein the post oxidation zone **90** comprises at least one post oxidation device; wherein the carboxylic acid slurry comprises at least one carboxylic acid; and wherein the post oxidation product **120** has a b* color of less than 4.5.

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This oxidizing step and the post oxidation zone are described subsequently in this disclosure.

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In another embodiment of the invention, a process to produce a crystallized product **180** is provided as shown in Figure 1. The process comprises the following steps.

Step (a) comprises oxidizing the crude carboxylic acid slurry **30** in a post oxidation zone **90** in the presence of steam **100** to form a post oxidation product **120**. Generally, the crude carboxylic acid slurry **30** is produced by oxidizing in a primary oxidation zone **20** an aromatic feed stock **10**. The primary oxidation zone **20** comprises at least one oxidation reactor, and the crude carboxylic acid slurry **30** comprises at least one carboxylic acid.

The oxidizing in the primary oxidation zone **20** is completed under reaction conditions, which produces a crude carboxylic acid slurry **30** from an aromatic feedstock **10**. Typically, the crude carboxylic acid slurry **30** comprises at least one carboxylic acid. Generally, the carboxylic acid is terephthalic acid.

Therefore, when terephthalic acid is utilized, the crude carboxylic acid slurry **30** would be referred to as crude terephthalic acid slurry.

However, suitable carboxylic acids include, but are not limited to, terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, and mixtures thereof. Crude terephthalic acid slurry is conventionally synthesized via the liquid phase oxidation of paraxylene in the presence of metal oxidation catalyst. Suitable catalysts include, but are not limited to, cobalt, manganese and bromide compounds, which are soluble in the selected solvent. Suitable solvents include, but are not limited to, aliphatic mono-carboxylic acids, preferably containing 2 to 6 carbon atoms, or benzoic acid and mixtures thereof and mixtures of these compounds with

water. Preferably, the solvent is acetic acid mixed with water in a ratio of about 5:1 to about 25:1, preferably between about 10:1 and about 15:1. However, it should be appreciated that other suitable solvents, such as those disclosed herein, may also be utilized. Patents disclosing the production of terephthalic acid, such as 4,158,738 and 3,996,271, are hereby incorporated by reference.

In cases where the carboxylic acid is terephthalic acid, the primary oxidation zone **20** has a water concentration less than about 10 wt%, preferably the water concentration is less than about 8 wt%, and most preferably the water concentration is less than about 6 wt%.

The post oxidation zone **90** comprises at least one post oxidation device. The crude carboxylic acid slurry **30** is fed to the post oxidation zone **90**. The post oxidation zone **90** comprises at least one post oxidation device. The term post oxidation means that the oxidation occurs after the primary oxidation zone **20** discussed previously. For example, the post oxidation zone **90** can comprise post oxidation devices in series.

When the carboxylic acid is terephthalic acid, the crude carboxylic acid slurry **30** in the post oxidation device is heated with steam **100** to between about 180°C and about 280°C, preferably between about 190°C and about 240°C, and most preferably between 195 °C to 215°C and further oxidized with air or a source of molecular oxygen fed by line **115** to produce a post oxidation product **120**. The temperature is the internal temperature of the post oxidation device. When the post oxidation zone

comprises more than one post oxidation device, the temperature can vary within the specified range for each post oxidation device. The steam **100** can be fed in the post oxidation zone **90** by any means known in the art. For example, a connection can be made for the steam **100** to be directly fed to the acetic acid vapor line. So the steam could be injected into the digester through the sparge ring. In addition to using steam, the post oxidation zone **90** can be heated with acetic acid vapor.

Additional air or molecular oxygen may be fed to the post oxidation zone **90** in an amount necessary to oxidize a substantial portion of the partially oxidized products and 4-carboxybenzaldehyde (4-CBA) in the crude carboxylic acid slurry **30** to the corresponding carboxylic acid. Generally, at least 70% by weight of the 4-CBA is converted to terephthalic acid in the post oxidation zone **90**. Preferably at least 80% by weight of the 4-CBA is converted to terephthalic acid in the post oxidation zone **90**. 4-carboxybenzaldehyde and p-toluic acid in high enough concentrations in the terephthalic acid product can be particularly detrimental to polymerization processes as they act as a chain terminator during the condensation reaction between terephthalic acid and ethylene glycol in the production of PET and can be detrimental to the performance of terephthalic acid hydrogenation processes. Typical terephthalic acid product contains on a weight basis less than 500 parts per million (ppm) 4-carboxybenzaldehyde and less than 250 ppm p-toluic acid. Preferably, the post oxidation zone is operated at a temperature and pressure sufficient

that the b^* color of the post oxidation product **120** ranges from about 0.5 to about 4.5.

Step (b) comprises purifying the post oxidation product before or after a crystallization zone to form a decolorized post oxidation product
5 having b^* color of less than 4.5.

The purifying of the post oxidation product can be accomplished by any means known in the art. For example colored impurities from the benzil, anthroquinone, and fluorenone families can be hydrogenated to colorless products. In addition any amount of process steps can be
10 between the post oxidation zone and the purifying of the post oxidation product and the isolation or recovery of the post oxidation product if desired.

The b^* color of the post oxidation product in conduit **120** is between about 0.5 to about 4.5. Preferably, the b^* color of the decolorized post
15 oxidation product in conduit **120** is between 0.5 to 2.0. Most preferably, the b^* color in the decolorized post oxidation product in conduit **120** is between 0.5 to 1.5. The b^* color is one of the three-color attributes measured on a spectroscopic reflectance-based instrument. The color can be measured by any device known in the art. A Hunter Ultrascan XE instrument is
20 typically the measuring device. Positive readings signify the degree of yellow (or absorbance of blue), while negative readings signify the degree of blue (or absorbance of yellow).

Offgas from the post oxidation zone is withdrawn via line **80** and fed to a recovery system where the solvent is removed from the offgas. The solvent comprising volatile organic compounds (VOCs). The VOCs and any hazardous pollutants may be incinerated.

- 5 Step (c) comprises crystallizing the post oxidation product **120** in the crystallization zone **160** to form a crystallized product **180**; wherein the crystallized product **180** has a b* color of less than 4.5.

 Generally, the crystallization zone **160** comprises at least one crystallizer. Vapor product from the crystallization zone **160** is withdrawn via
10 line **130**, condensed in a condenser zone **170**, which comprises at least one condenser and returned to the crystallization zone **160**. Optionally, the liquid in conduit **140** or vapor **130** in the condenser zone **170** can be recycled, or it can be withdrawn or sent to an energy recovery device. In addition, the liquid crystallization offgas **150** from the condenser zone **170** is
15 removed via line **150** and can be routed to a recovery system where the solvent is removed and crystallization offgas **150** comprising VOCs and pollutants are burned.

 When the carboxylic acid is terephthalic acid, the post oxidation product **120** from the post oxidation zone **90** is withdrawn via line **120** and
20 fed to a crystallization zone **160** comprising at least one crystallizer where it is cooled to a temperature between about 110°C and about 190°C to form a crystallized product **180**, preferably to a temperature between about 140°C to about 180°C, most preferably 150°C to 170°C. Preferably, the b* color of

the crystallized product in conduit **180** is between about 0.5 to about 4.5.

More preferably, the b^* color of the crystallized product in conduit **180** is between 0.5 to 2.0. Most preferably, the b^* color in the crystallized product in conduit **180** is between 0.5 to 1.5

- 5 The crystallized product **180** from the crystallization zone **160** is withdrawn via line **180**. Typically, the crystallized product **180** is then fed directly to a vessel and cooled to form a cooled crystallized product. When the carboxylic acid is terephthalic acid, the cooled crystallized product is cooled in a vessel to typically a temperature of approximately 90° C or less
- 10 than before being introduced into a process for recovering the carboxylic acid as a dry powder or wet cake.

EXAMPLES

The invention has been described in detail with particular reference
5 to preferred embodiments thereof, but it will be understood that variations
and modifications can be effected within the spirit and scope of the
invention.

Example 1

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In a plant trial, steam was used in the heating of a post oxidation
device. The temperature of the post oxidation device was operating at
about 195°C to about 215°C. The airflow was set at a ratio of about 3.8 kg
air/ton crude carboxylic acid slurry. The steam flow to the post oxidation
15 device was between about 6.5 to about 8.2 metric tons/hour. An overall
reduction in energy of 0.3 GJ/ton for producing terephthalic acid was
observed. This represents a 5% reduction in energy versus operating
without the use of steam to the post oxidation device. The acid burn and
decomposition in the post oxidation device decreased due to the injection of
20 steam into the post oxidation device. The acid loss (acetic acid/ton post
oxidation product) dropped about 10%. Therefore, both reduction in energy
consumption and acid burn were observed through the use of steam to heat
the post oxidation device.

WE CLAIM:

1. A process to produce a post oxidation product comprising the
5 following steps:
 - (a) oxidizing in a post oxidation zone a crude carboxylic acid slurry in the presence of steam to form said post oxidation product; wherein said post oxidation zone comprises at least one post oxidation device; wherein said crude carboxylic acid slurry comprises at least one carboxylic
10 acid;
 - (b) purifying said post oxidation product to form a decolorized post oxidation product having b* color of less than 4.5.
2. A process according to claim 1 where said decolorized post oxidation product has a b* color less than 3.5.
- 15 3. A process according to claim 1 wherein said carboxylic acid is selected from the group consisting of terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, and mixtures thereof.
4. A process according to claim 1 wherein said carboxylic acid is terephthalic acid.
- 20 5. A process according to claim 4 wherein said steam is used to heat said post oxidation zone to a temperature in a range from about 180°C to about 280 °C.

6. A process according to claim 5 wherein said post oxidation zone is operated at a pressure of about 10 barg to about 50 barg.

7. A process to produce a crystallized product said process comprising the following steps:

5 (a) oxidizing in a post oxidation zone said crude carboxylic acid slurry in a post oxidation zone in the presence of steam to form a post oxidation product and an offgas stream; wherein said post oxidation zone comprises at least one post oxidation device;

(b) purifying said post oxidation product before or after a
10 crystallization zone to form a decolorized post oxidation product having b* color of less than 4.5; and

(c) crystallizing in said crystallization zone said post oxidation product ; wherein said crystallization zone comprises at least one crystallizer.

15 8. A process according to claim 7 wherein said purified post oxidation product has a b* color of less than 3.

9. A process according claim 7 wherein said carboxylic acid is selected from the group consisting of terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, and mixtures thereof.

20 10. A process according to claim 7 wherein said carboxylic acid is terephthalic acid.

11. A process according to claim 10 wherein said steam is used to heat the post oxidation zone to a temperature in a range from about 180°C to about 280°C.
12. A process according to claim 11 wherein said post oxidation zone is
5 operated at a pressure of about 10 barg to about 50 barg.
13. The process according to claim 10 wherein said crystallizer is operated at a temperature between about 140°C and 190°C .
14. A process to produce a post oxidation product comprising oxidizing in a post oxidation zone a crude carboxylic acid slurry in the presence of
10 steam to form said post oxidation product; wherein said crude carboxylic acid slurry comprises terephthalic acid; wherein said post oxidation zone comprises at least one post oxidation device; wherein said post oxidation product has a b* color of less than about 4.5.
15. A process according to claim 14 wherein said steam is used to heat
15 the post oxidation zone to a temperature in a range from about 180°C to about 280°C.
- 16 A process according to claim 15 wherein said post oxidation zone is operated at a pressure of about 10 barg to about 50 barg.
17. A process to produce crystallized product said process comprising
20 the following steps:
- (a) oxidizing said crude carboxylic acid slurry in a post oxidation zone in the presence of steam to form a post oxidation product; wherein

said post oxidation zone comprises at least one post oxidation device;
wherein the pressure of said post oxidation zone is between about 10 barg
to about 50 barg; and

- (b) crystallizing in a crystallization zone said post oxidation
5 product to form a crystallized product; wherein said crystallization zone
comprises at least one crystallizer; wherein said crystallizer is operated at a
temperature between about 140°C and 190°C ; and wherein said
crystallized product has a b* color of less than 4.5.

18. A process according to claim 17 where said crystallized product has
10 a b* color of less than 3.