(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 February 2009 (26.02.2009)

PCT

(10) International Publication Number
WO 2009/024872 A2

(51) International Patent Classification:
C07C 51/43 (2006.01) *C07C 63/26* (2006.01)
C07C 51/47 (2006.01) *C07C 63/307* (2006.01)
C07C 63/24 (2006.01)

(21) International Application Number:
PCT/IB2008/003093

(22) International Filing Date: 16 May 2008 (16.05.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/932,447 31 May 2007 (31.05.2007) US

(71) Applicant *(for all designated States except US)*: **DOW ITALIA S.R.L.** [IT/IT]; 2040 Dow Center, Midland, MI (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **BALDELLI, Alessandro** [IT/IT]; Via D. Alighieri, 43, I-20047 Brughe-rio (IT). **CATTANEO, Carlo** [IT/IT]; Via A. Costa, 4, I-20131 Milan (IT). **COCCO, Giovanni** [IT/IT]; Via Gioberti, 6, I-09170 Oristano (IT). **GNAGNETTI, Andrea** [IT/IT]; Via F. Cavallotti, 98, I-20052 Monza - MI (IT). **MONAGHEDDU, Marzio** [IT/IT]; Via Case Ferrovieri Porta Nuova 20, I-37138 Verona (IT). **PIRAS, Luciano** [IT/IT]; Via Sporting Mirasole, 44, I-20090 Opera - MI (IT).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

WO 2009/024872 A2

(54) Title: IMPROVED PROCESS FOR THE RECOVERY OF TEREPHTHALIC ACID

(57) Abstract: A method for the recovery of carboxylic acid is disclosed. The method comprises the steps of introducing a liquid slurry comprising water, crystallized carboxylic acid such as terephthalic acid, isophthalic acid, trimellitic acid, and impurities into a high pressure rotary filter; filtering said slurry and collecting at least some of the solid portion; passing the collected solid portion to a rotary valve comprising a temperature control system; controlling the temperature in the rotary valve through the temperature control system; and removing the solid portion from the rotary valve. The rotary valve comprises a valve case and a rotor, and the temperature control system controls the temperature difference between the valve case and the rotor.

IMPROVED PROCESS FOR THE RECOVERY OF TEREPHTHALIC ACID

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of United States Provisional Application Number 60/932,447, May 31, 2007.

The present invention relates to a new process for the recovery of poly carboxylic acids such as purified terephthalic acid ("PTA"), purified isophthalic acid and trimellitic acid. More particularly, this application relates to the novel use of a rotary pressure filter to recover crystalline terephthalic acid, isophthalic acid and trimellitic acid and a process to recover the resulting crystals.

BACKGROUND

For sake of simplicity the background will focus on terephthalic acid. Terephthalic acid is used in the production of many different polymers, including polyethylene terephthalate (PET). The typical process for PET is the direct condensation of terephthalic acid with a polyalcohol. This direct esterification reaction requires purified terephthalic acid, for the reaction product to be acceptable.

Terephthalic Acid is produced by direct oxidation of *p*-xylene and subsequent crystallization from the mother liquor to recover the Crude Terephthalic Acid (CTA). This CTA still contains approximately 0.2-0.4 percent by weight of 4-carboxybenzaldehyde (4-CBA) as major impurity. To reduce the content of 4-CBA, the CTA is typically dissolved in water and then the resulting solution is treated in a hydrogenation reactor, to convert the 4-CBA into p-toluic acid. The solution from the hydrogenation reactor is then typically cooled by flash in a battery of crystallizers to precipitate the purified terephthalic acid (PTA) as a crystal. The slurry coming from the crystallizers still contains a significant amount of p-toluic acid that needs to be separated from PTA, to meet the usual commercial specification of no more that 150 ppm.

In order to purify the PTA two subsequent stages of solid separation are most currently used. The traditional method to separate the PTA from its mother liquor consists in centrifuging the slurry at a temperature of from 100°C to 170°C and a pressure of from 1

to 7 bar. Under these conditions the majority of the p-toluic acid will remain in solution, allowing it to be separated.

The crystals of PTA coming from the centrifuge contain only a small amount of p-toluic acid, but do contain residual mother liquor (typically 10-15 percent). To get rid of these impurities, the crystals are usually mixed with additional water, typically in a ratio of 1.1 to 1.5 m^3 water/ton PTA, to wash the mother liquor still entrained. This results in a slurry having a 45 (±5) percent solids. This slurry is then flashed to atmospheric pressure and fed either to a second stage of centrifuges or to Rotary Vacuum Filters (RVF). The PTA, containing a residual 10-15 percent of water, is then dried, typically in a rotary dryer, and stored. The PTA crystals still contain minor amounts of p-toluic acid (usually less than 150 ppm) while 4-CBA content is typically lower than 25 ppm.

U.S. Patent 5,175,355 teaches a method of purifying the terephthalic acid comprising pressure filtering. This reference teaches introducing an aqueous slurry (comprising purified terephthalic acid present as crystals and p-toluic acid present in the aqueous solution and as a co-crystallized form) into one or more filter cells. The slurry is filtered at a system pressure of from atmosphere to 16 atm. The filter cell with the resulting filter cake is then transported into a wash zone where a stream of water heated to 38°C to 205°C is introduced to the filter cell to form a reservoir of water over the filter cake. Displacement washing is then achieved by forcing the water through the cake at a pressure gradient, which is at least 0.5 atm above the system pressure while maintaining the reservoir. The displacement washing is allowed to continue for a sufficient time to remove a desired amount of impurities. The filter cell is then transported to a pressure release zone wherein the system pressure is quickly released to flash evaporate the water remaining in the filter cake and the product is recovered. The pressure release zone is then pressurized back up to the system pressure so as to be ready to accept additional product. This process reportedly results in terephthalic acid that contains less than 200 ppm by weight of p-toluic acid.

U.S. Patent No. 6,639,104 describes an improved process comprising transferring the washed filter cake to a letdown zone (or pressure release zone) which is at a pressure less than the pressure of the washing zone. This reference describes a dome valve as a specific embodiment of a letdown system that may be used.

Other references describing methods for purifying or recovering materials from crystal-containing slurries include WO 0155075, US 6,655,531, US 5,470,473, US 5,093,001, EP 0 406 424, WO 9519335, and JP 11179115.

It would be an advance in the art of the production of purified terephthalic acid to provide an improved process for the recovery of terephthalic acid and removal of impurities from purified terephthalic acid crystals.

SUMMARY OF THE INVENTION

The present invention is an improved method for the recovery of polycarboxylic acids such as purified terephthalic acid ("PTA"), purified isophthalic acid and trimellitic acid, which comprises a) introducing a liquid slurry comprising water, crystallized terephthalic acid, and impurities into a high pressure rotary filter; b) filtering said slurry and collecting at least some of the solid portion; c) passing the collected solid portion to a rotary valve comprising a temperature control system; d) controlling the temperature in the rotary valve through the temperature control system; and e) removing the solid portion from the rotary valve. The rotary valve comprises a valve case and a rotor, and the temperature control system controls the temperature difference between the valve case and the rotor.

The present invention provides an improved system for recovery of polycarboxylic acids, utilizing a letdown system that allows for depressurizing the solid material without affecting the filter pressure control system or material throughput.

DETAILED DESCRIPTION OF THE INVENTION

For the present invention, the liquid slurry containing the carboxylic acid such as terephthalic acid, isophthalic acid, trimellitic acid containing the impurities can come from any terephthalic acid, isophthalic acid, trimellitic acid production scheme. These are known in the art and are of minimal importance to the invention at hand. The particular high-pressure rotary filter used to filter the slurry is similarly not critical to the present invention. Any filtering system capable of operating at a pressure greater than atmospheric pressure may be used. Preferably, for standard operating conditions, the filter is capable of handling the full throughput of terephthalic acid of the plant, and capable of operating under pressures of from 1.0 to 10.0 bar. A suitable filter is the Bird Young Rotary Filter sold by

Andritz and described in U.S. Patent Nos. 5,70,473 and 6,655,531, incorporated herein by reference.

The filter typically consists of a case, pressurized at process pressure, and a drum covered by a filtering device such as a cloth or equivalent filtering device, pressurized at a pressure suitably lower than the case.

The drum is ideally divided into three zones:

- First zone, where the mother liquor is removed.
- Second zone, where the solid is washed.
- Third zone, where the excess of washing liquor is removed and the solid is discharged.

The pressure of the case is preferably in a range of from1.5 to 6.5 bar, with about 4.5 bar being most preferred. The case of the filter is pressurized with hot inert gas, steam or a mixture of the two, useful for pressurizing filter case. Using hot gas, steam or a mixture of the two for pressurization allows an uniform temperature inside the filtration device so avoiding cold spot that can cause local crystallization of impurities, and then decrease the product quality. The filtering is carried out at a temperature of from 110 to 160 °Cwith 147°C being most preferred.

The slurry, having a temperature from 110 to 160 °C, more preferably from 135 to 150 °C, and even more preferably 147 °C, is fed from the last crystallizer of the crystallization unit to a feed slurry basin inside the filter case in such a way that an amount from 20% to 100% of the fed slurry overflows to a hydraulic seal, comprising a pressure vessel with a level control system, which pressure is balanced with the filter case through the overflow line itself. This embodiment allows keeping constant the feed to the filter, the submergence of the filtering drum and the pressure of the filtration device and then back to the slurry feeding vessel.

The pressure difference between case and drum is in the range of 0.1 to 2.0 bar, preferably in the range of 0.3 to 0.7 bar, most preferably 0.5 bar.

The mother liquor removed from the rotary pressure filter can be separately recovered and reused into the production process or sent to waste treatment facilities, as is known in the art.

The remaining solid portion is then washed with additional amounts of water. It has been discovered that less wash water is required in the present process to achieve purity similar to the traditional methods. Thus while any amount of water may be used in the washing stage of the present invention, it is preferred that less than 1 cubic meter per ton of PTA be used, in order to conserve water and reduce the energy associated to heating up this water to process temperature. The water amount is preferably in a range of from 0.2 to 0.7 m^3/MT of PTA, with about 0.5 m^3/MT of PTA being most preferred. The washing is preferably done at the same temperature as the filtering, although this is for convenience and is not mandatory. The temperature of the water used to wash the solid material is in the range of 50°C to 161°C, preferably in the range of 130°C to 150°C, most preferably 147°C. The wash liquor can then be separately collected from the mother liquor and reused into the production process or recycled back into the production process, as is known in the art.

After washing, the solid material is is detached by the cake removal system blowing hot gas, steam or a mixture of the two from the internal side of the rotating drum into the filter case, as it is known in the art, being the blowing fluid temperature in the range from 110 to 160 °C, more preferably from 135 to 150 °C, and even more preferably 147 °C. Feeding the cake removal system with hot gas, allows maintaining the temperature of the discharged product suitably high, so making the eventually following drying operation easier and cheaper. The detached solid is preferably passed through a let down system including a rotary valve into an atmospheric cake hopper, which is at a pressure that is less than the filter case.

The letdown system of the present invention is a rotary valve with appropriate clearance between the vanes and the case, such that vanes do not sealingly engage the inside surfaces of the rotary valve case. One example of a rotary valve useful for the present invention is described in US 2006/0045729. For purposes of the present invention, the rotary valve comprises at least a valve case and a rotor. The rotary valve is also equipped with a temperature control system configured so as to maintain the temperature difference between case and rotor of the rotary valve according to a chosen set point so controlling the clearance between the vanes and the case of the rotary valve. In this manner, the rotary valve allows the moisture present in the sold product to be released smoothly as vapors in the vanes of the valve itself and then the sudden flash on the discharge side of the valve is avoided. Therefore, the temperature control system acts as in indirect control of the

clearance between the rotor and the valve case, indirectly resulting in a controlled pressure drop profile.

The temperature control system used to control the temperature difference between the valve case and rotor comprises at least one heating medium, at least one temperature measuring device and at least one logic control device. The heating medium used is not critical and can be, for example, hot steam, hot nitrogen, off-gas coming from the oxidation reactor, any other suitable hot inert gas, an electrical heating apparatus, or a combination of one or more of these.

The application of this novel system allowing release of the moisture in the solid product does not avoid, but control the gas leakage. Having a continuous gas leakage through the rotary valve requires the use of hot gas for pressurization of the filter; as a matter of fact cold gas can create problems in controlling the temperature of the system either increasing the gas leakage or causing seizing of the valve. This novel system, together with the use of hot pressurizing fluid, allows limiting and controlling the gas leakage through the valve and preventing seizing.

The cake hopper, receiving the solid product from the let down system, is optionally equipped with two outlets for releasing gaseous material and is connected from one side to a vacuum system to prevent undesired pressure increase, and to an atmospheric buffer from another side to prevent undesired full vacuum conditions.

The solid material can then be passed to a drier by means of a suitable device, such as a screw, for further processing as is known in the art.

EXAMPLES

The following procedures are used in Examples 1 and 2:

Procedure for determining moisture content

A Petri dish is dried in an oven at approximately 105°C until it is a constant weight. About 10 grams of sample is weighed to the nearest 0.1 mg into the dried Petri dish. The Petri dish containing the sample is put into an air oven at approximately 105°C for 2 hours and cooled at room temperature in a dryer. The Petri dish is then weighed for a first weight reading. The Petri dish containing the sample is dried in the oven for 30 minutes more and cooled at room temperature in a dryer. The Petri dish is then weighed for a second weight reading. The first and second weight readings are compared. A difference of less than 0.5 milligrams

is considered constant. Otherwise, the drying is completed until the weight difference is constant.

P-toluic aid concentration is determined using HPLC (Hitachi, model L-7100 or equivalent).

Examples 1 and 2

Examples 1 and 2 demonstrate the effect of varying the valve conditions and the pressurizing gas on the moisture and p-toluic acid content in the product. The results from Examples 1 and 2 are summarized below in Table 1.

Table 1

Example	1	2
Filter Conditions:		
Case pressure (bar)	3	3
Case-Drum pressure differential (bar)	0.3	0.3
Pressurizing gas flow (kg/hr)	790	530
Filtered solid feed (kg/hr)	1200	1200
Slurry temperature (°C)	125.3	128.3
Washing water (kg/hr)	510	510
Washing water temperature (°C)	125	126
Rotary valve case temperature (°C)	56	85
Rotary valve rotor temperature (°C)	71	124
Rotary valve gas leakage (kg/hr)	430	265
Product quality:		
Moisture content (%)	11.8	8.1
p-toluic acid in wet cake (ppm)	183	153

WHAT IS CLAIMED IS:

1. A process for the preparation of purified carboxylic acid which comprises:

a. introducing a liquid slurry comprising water, crystallized carboxylic acid, and impurities into a high pressure rotary filter;

b. filtering said slurry and collecting at least some of the solid portion;

c. passing the collected solid portion to a rotary valve comprising a temperature control system;

d. controlling the temperature in the rotary valve through the temperature control system; and

e. removing the solid portion from the rotary valve.

2. The process according to Claim 1 wherein the carboxylic acid is terephthalic acid, isophthalic acid, or trimellitic acid.

3. The process according to Claim 1 or 2 wherein the high pressure rotary filter used in step a is pressurized with a hot fluid.

4. The process according to Claim 3 wherein the hot fluid is at a temperature of from 110°C to 160°C.

5. The process according to Claim 3 or 4 wherein the hot fluid comprises steam, not nitrogen, hot off-gas coming from an oxidation reactor, or a combination thereof.

6. The process according to Claim 1 wherein the rotary valve comprises a valve case and a rotor.

7. The process according to Claim 6 wherein, in step d, the temperature control system controls the temperature difference between the valve case and the rotor.

8. The process according to any of Claims 1 through 7 wherein the temperature control system comprises at least one heating medium, at least one temperature measuring device and at least one logic control device suitable for controlling the temperature difference between the valve case and the rotor.

9. The process according to Claim 8 wherein the heating medium is selected from the group consisting of hot steam, hot nitrogen, off-gas coming from the carboxylic acid oxidation reactor, any other suitable hot inert gas, an electrical heating apparatus, and combinations thereof.