



(51) International Patent Classification:

C07C 67/08 (2006.01) C07C 69/82 (2006.01)  
C07C 69/80 (2006.01)

(21) International Application Number:

PCT/IB2016/057939

(22) International Filing Date:

22 December 2016 (22.12.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/272,402 29 December 2015 (29.12.2015) US

(71) Applicant: SABIC GLOBAL TECHNOLOGIES B.V.  
[NL/NL]; Plasticslaan 1, 4612 PX Bergen op Zoom (NL).

(72) Inventors: NANDY, Ritesh; Millers Boulevard 70/2,  
Millers Road, Bangalore 560052 (IN). VISHAL, Patrick;  
Millers Boulevard 70/2, Millers Road, Bangalore 560052  
(IN). NESAKUMAR, Edward Joseph; Millers Boulevard  
70/2, Millers Road, Bangalore 560052 (IN).

(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, BN, BR, BW, BY,  
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM,  
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,

HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN,  
KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA,  
MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG,  
NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS,  
RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY,  
TH, 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, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,  
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,  
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,  
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,  
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,  
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a  
patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the  
earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))

(54) Title: PROCESS FOR THE PREPARATION OF A DIALKYL ARYLATE

(57) Abstract: A process for the preparation of a dialkyl arylate includes reacting an aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof with a C<sub>5-13</sub> alcohol in the presence of an acid catalyst to provide a reaction mixture comprising the dialkyl arylate. The acid catalyst can include sulfuric acid, a sulfonic acid, or a combination including at least one of the foregoing, and can be present in an amount of 0.1 to 0.5 mole percent, based on the moles of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof. The aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof and the C<sub>5-13</sub> alcohol are present in a molar ratio of at least 1:2.2.



## PROCESS FOR THE PREPARATION OF A DIALKYL ARYLATE

## BACKGROUND

[0001] Dialkyl arylates are used as plasticizers to increase the flexibility, distensibility, and workability of polymers such as polyvinyl chloride (PVC). Dialkyl arylates of particular interest are di(C<sub>1-13</sub>alkyl) arylates such as diisooctyl terephthalate (DOTP, also known as di-2-ethylhexyl phthalate (DEHP)), and diisooctyl phthalate (DOP, also known as di-2-ethylhexyl phthalate (DEHP) and bis(2-ethylhexyl) phthalate). DOTP and DOP can be used as a plasticizer in a wide variety of applications, such as coating compositions, sealing compositions, and rubber, particularly PVC articles.

[0002] As is known in the art, longer-chain dialkyl arylates, e.g., di(C<sub>5-13</sub>alkyl) terephthalates such as DOTP, are generally synthesized by a titanate-catalyzed transesterification, for example transesterification of dimethyl terephthalate (DMT) with 2-ethylhexanol. Another route includes the titanate-catalyzed esterification of terephthalic acid with 2-ethylhexanol. However, there are significant process limitations associated with the above-described procedures, in particular for dialkyl terephthalates such as DOTP, using titanium-containing catalysts. For example, esterification of terephthalic acid and with 2-ethylhexanol can be slow, and generally produce significant amounts of foaming. Other drawbacks include the incomplete conversion of terephthalic acid to DOTP. Unreacted terephthalic acid must be separated by filtration prior to downstream purification and isolation of DOTP.

[0003] Accordingly, there is a continuing need for an improved process for the preparation of di(C<sub>5-13</sub>alkyl) arylates, in particular di(C<sub>5-13</sub>alkyl) terephthalates such as DOTP, that overcomes the above-described technical limitations.

## BRIEF DESCRIPTION

[0004] A process for the preparation of a di(C<sub>5-13</sub>alkyl) arylate comprises reacting an aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof with a C<sub>5-13</sub> alcohol in the presence of an acid catalyst comprising sulfuric acid, a sulfonic acid, or a combination comprising at least one of the foregoing, to provide a reaction mixture comprising the di(C<sub>5-13</sub>alkyl) arylate; wherein the acid catalyst is present in an amount of 0.1 to 0.5 mole percent, based on the moles of the aromatic acid; and the aromatic acid and the C<sub>5-13</sub> alcohol are present in a molar ratio of at least 1:2.2.

[0005] A process for the preparation of diisooctyl terephthalate comprises reacting terephthalic acid with 2-ethylhexanol in the presence of an acid catalyst comprising sulfuric acid, a sulfonic acid, or a combination comprising at least one of the foregoing to provide a reaction mixture comprising the diisooctyl terephthalate; wherein the acid catalyst is present in an amount of 0.2 to 0.5 mole percent, based on the moles of the terephthalic acid; and the terephthalic acid and the 2-ethylhexanol are present in a molar ratio of 1:2.2 to 1:4.

[0006] The above described and other features are exemplified by the following detailed description.

#### DETAILED DESCRIPTION

[0007] A process for the preparation of a di(C<sub>5-13</sub>alkyl) arylate, in particular a di(C<sub>5-13</sub>alkyl) terephthalate such as DOTP, is disclosed herein. It has been unexpectedly discovered that use of a particular amount of certain acid catalysts can provide the desired di(C<sub>5-13</sub>alkyl) arylate with improved selectivity, conversion, and color of the final product. In a further advantageous feature, no foaming or frothing was observed during the process. In contrast, syntheses of di(C<sub>5-13</sub>alkyl) arylates using titanium-containing catalysts can exhibit significant frothing, causing difficulty in removing water from the reaction. Furthermore, the homogenous reaction mixture achieved in the presence of these acid catalysts simplifies the isolation procedure.

[0008] Accordingly, a process for the preparation of a di(C<sub>5-13</sub>alkyl) arylate, in particular a di(C<sub>5-13</sub>alkyl) terephthalate such as DOTP, comprises reacting an aromatic acid, or its corresponding anhydride or di(C<sub>1-3</sub>alkyl)ester, with a C<sub>5-13</sub> alcohol in the presence of an acid catalyst comprising sulfuric acid, a sulfonic acid, or a combination comprising at least one of the foregoing to provide a reaction mixture comprising the di(C<sub>5-13</sub>alkyl) arylate, in particular the di(C<sub>5-13</sub>alkyl) terephthalate.

[0009] “Dialkyl arylate” as used herein is a shorthand term used for convenience in referring to di(C<sub>5-13</sub>alkyl) esters of aromatic diacids as described in further detail below, specifically di(C<sub>7-10</sub>alkyl) esters of aromatic diacids. In an embodiment, the di(C<sub>5-13</sub>alkyl) arylate is a di(C<sub>5-13</sub>alkyl) phthalate, where “phthalate” refers to the ortho-isomer of dicarboxybenzene, or a di(C<sub>5-13</sub>alkyl) terephthalate, where “terephthalate” refers to the para-isomer of dicarboxybenzene. In some embodiments the dialkyl arylate is diisooctyl terephthalate or diisooctyl phthalate. As is known in the art, compounds designated terephthalates or phthalates can nonetheless contain minor amounts of various isomeric species, such as the esters of phthalic acid, isophthalic acid, and terephthalic acid, or alkyl groups that are

straight-chain or have other branching. The terms “diisooctyl terephthalate” and “diisooctyl phthalate” as used herein are intended to include such isomeric variations.

[0010] The dialkyl arylate can contain the residue of an aromatic acid, anhydride or di(C<sub>1-3</sub>alkyl)ester such as phthalic acid, phthalic anhydride, dimethyl or diethyl phthalate, isophthalic acid, dimethyl or diethyl isophthalate, terephthalic acid, terephthalic anhydride, dimethyl or diethyl terephthalate, trimesic acid, trimellitic acid, trimellitic anhydride, trimethyl or triethyl mesylate, pyromellitic acid, pyromellitic anhydride, benzophenonetetracarboxylic acid, benzophenonetetracarboxylic anhydride, or a combination comprising at least one of the foregoing acids, anhydrides, or diesters. In some embodiments, one or more other carboxylic acids, anhydrides, or diesters can be present, for example an aromatic monocarboxylic acid such as benzoic acid or its (C<sub>1-3</sub>alkyl)ester; an aliphatic di- or tricarboxylic acid such as succinic acid, adipic acid, trimethyl adipic acid, sebacic acid, azelaic acid, suberic acid, decanedioic acid, brassylic acid, dodecanedioic acid, or citric acid or the corresponding di- or tri(C<sub>1-3</sub>alkyl)ester; or an unsaturated aliphatic di- or tricarboxylic acid such as maleic acid or fumaric acid or the corresponding di- or tri(C<sub>1-3</sub>alkyl)ester; or an aliphatic long-chain monocarboxylic acid or corresponding (C<sub>1-3</sub>alkyl)ester such as oleic acid or stearic acid or corresponding (C<sub>1-3</sub>alkyl)ester. In some embodiments, only phthalic acid or the anhydride or di(C<sub>1-3</sub>alkyl)ester thereof, isophthalic acid or the anhydride or di(C<sub>1-3</sub>alkyl)ester thereof, or terephthalic acid or the anhydride or di(C<sub>1-3</sub>alkyl)ester thereof, or a combination comprising at least one of the foregoing is present. In some embodiments, the dialkyl arylate comprises the residue of an aromatic diacid, aromatic dianhydride, or dialkyl ester thereof. In a preferred embodiment, the dialkyl arylate comprises the residue of terephthalic acid, diterephthalic anhydride, or dimethyl or diethyl terephthalate with low (e.g., less than 10 weight percent (wt%)) amounts of phthalic acid or phthalic anhydride.

[0011] The dialkyl arylate can further comprise the residue of a C<sub>5-13</sub> alcohol. Examples of the alcohol include a saturated, monohydric aliphatic alcohol such as normal- or iso-pentanol, normal- or iso-hexanol, normal- or iso-heptanol, normal- or iso-octanol, 2-ethylhexanol, normal- or iso-nonyl alcohol, normal- or iso-decanol, 2-propyl heptanol, normal- or iso-undecanol, or normal or iso-dodecanol, or normal- or iso-tridecanol; a polyhydric aliphatic alcohol such as ethylene glycol, propylene glycol, or their dimers, trimers, or tetramers; or a combination comprising at least one of the foregoing. C<sub>5-12</sub> alcohols are preferably employed, and the C<sub>7</sub> to C<sub>10</sub> alcohols, especially the C<sub>8</sub> alcohols are preferred in the production of dialkyl arylates.

[0012] In some embodiments, the C<sub>5-13</sub> alcohol can comprise hexanol, cyclohexanol, heptanol, 2-ethylhexanol, cyclohexanemethanol, methylcyclohexanemethanol (including cis and

trans isomers, as well as the 1,2-, 1,3-, or 1,4-isomers), n-octanol, iso-octanol, nonanol, decanol, 2-propyl heptanol, benzyl alcohol, 2-phenyl ethanol, or a combination comprising at least one of the foregoing. For example, the C<sub>5-13</sub> alcohol can be 2-ethylhexanol. In an embodiment, when the C<sub>5-13</sub> alcohol is 2-ethylhexanol, the dialkyl arylate is diisooctyl terephthalate.

[0013] The reaction between the aromatic acid, anhydride or di(C<sub>1-3</sub>alkyl)ester and the alcohol can be an esterification or a transesterification, depending on the starting material, and may be referred to collectively herein as an “esterification” for convenience. The reaction can be conducted in the presence of sulfuric acid, a sulfonic acid, or a combination comprising at least one of the foregoing. In some embodiments, the sulfonic acid is of the formula RSO<sub>3</sub>H wherein R is a C<sub>1-18</sub> hydrocarbyl group, preferably a C<sub>1-18</sub> alkyl, C<sub>1-18</sub> alkenyl, C<sub>6-18</sub> aryl, C<sub>7-18</sub> alkylenearyl (e.g., benzyl), or C<sub>7-18</sub> arylenealkyl (e.g., toluyl). Each of the foregoing groups can optionally be independently substituted with 1 to 3 groups, including halogen groups, nitrile groups, nitro groups, C<sub>1-6</sub> alkyl groups, C<sub>1-6</sub> alkoxy groups, phenyl, or phenoxy. In some embodiments the sulfonic acid is methanesulfonic acid, dodecyl benzene sulfonic acid, para-toluene sulfonic acid, or a combination comprising at least one of the foregoing. The indicated number of carbon atoms in the group includes any substituents. In some embodiments, the acid catalyst can be sulfuric acid, methanesulfonic acid, or a combination comprising at least one of the foregoing.

[0014] The aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester and the C<sub>5-13</sub> alcohol can be present in a molar ratio of at least 1:2.2, for example at least 1:3, for example at least 1:3.2, for example at least 1:3.5. In some embodiments, the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester and the C<sub>5-13</sub> alcohol are present in a molar ratio of 1:3 to 1:4.

[0015] The acid catalyst can be present in an amount of 0.1 to 0.5 mole percent, or 0.2 to 0.5 mole percent, based on the moles of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester. In some embodiments, the acid catalyst can be present in an amount of 0.2 to 0.35 mole percent, preferably 0.22 to 0.33 mole percent, based on the moles of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester. In an embodiment, the acid catalyst is sulfuric acid, methanesulfonic acid, or a combination comprising at least one of the foregoing present in an amount of 0.2 to 0.35 mole percent, based on the total moles of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester.

[0016] The reaction is carried out under conditions effective to provide the dialkyl arylate, in particular the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP. A variety of conditions can be suitable for the reaction, depending on the particular acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester, alcohol, desired efficiency, catalyst, and other considerations. For example, the reaction can be at a temperature of 180 to 230°C, for example 200 to 220°C, and a pressure of

0.3 to 2 bar. The reaction is preferably carried out at atmospheric pressure. Furthermore, the reaction can be for a desired period of time, for example 12 to 24 hours, for example 18 to 24 hours. The reaction can be conducted under an inert atmosphere with the concomitant removal of water (or as it is formed).

[0017] In some embodiments, the reaction mixture can comprise the dialkyl arylate, in particular the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP, residual C<sub>5-13</sub> alcohol, water (for example, as a byproduct of the esterification reaction), C<sub>1-3</sub> alcohol, or a combination comprising at least one of the foregoing. In some embodiments, the reaction mixture can be homogenous. For example, the reaction mixture can be a homogenous mixture when conversion of the aromatic dicarboxylic acid is greater than 90%, for example, greater than 95%.

[0018] The process further comprises isolating the dialkyl arylate, in particular, the di(C<sub>5-13</sub>alkyl) terephthalate, from the reaction mixture. Isolating the dialkyl arylate, in particular, the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP, can include a series of process steps including one or more of distillation, acid neutralization, and filtration. The reaction mixture can be distilled to remove at least a portion of the residual C<sub>5-13</sub> alcohol and the acid catalyst can be neutralized, providing a first intermediate mixture. In some embodiments, distilling the reaction mixture can be carried out prior to neutralizing the acid catalyst. In some embodiments, neutralizing the acid catalyst can be carried out prior to distilling the reaction mixture. Neutralization of the acid catalyst can be by addition of an aqueous alkaline solution, where the amount of aqueous alkaline solution that is added is generally equivalent to the amount of acid present in the reaction mixture. Exemplary bases suitable for use in the aqueous alkaline solution include alkali or alkaline earth metal salts, particularly sodium, potassium, or calcium salts such as sodium carbonate, potassium carbonate, or calcium carbonate, and alkali or alkaline earth metal hydroxides such as sodium hydroxide, potassium hydroxide, or calcium hydroxide, e.g., aqueous sodium hydroxide, potassium hydroxide, or calcium hydroxide. The first intermediate mixture can be further distilled to remove water and a final portion of the residual C<sub>5-13</sub> alcohol to provide a second intermediate mixture. The second intermediate mixture can be filtered to provide a filtrate comprising the dialkyl arylate, in particular, the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP. In some embodiments, isolating the dialkyl arylate, in particular the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP, further comprises treating the filtrate with activated charcoal, and filtering the treated mixture, for example using a filter aid, to provide the dialkyl arylate, in particular, the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP.

[0019] The process described herein can provide the dialkyl arylate, in particular, the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP, with a selectivity of greater than 95%, for

example, greater than 98%, for example, greater than 99%. A selectivity of greater than 95% means that the reaction mixture comprises the dialkyl arylate, in particular the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP, and less than 5 wt% of the corresponding monoester, based on the weight of the reaction mixture. Similarly, a selectivity of greater than 98% means that the reaction mixture comprises the dialkyl arylate, in particular the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP, and less than 2 wt% of the corresponding monoester, based on the weight of the reaction mixture, and a selectivity of greater than 99% means that the reaction mixture comprises the dialkyl arylate, in particular the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP, and less than 1 wt% of the corresponding mono(C<sub>5-13</sub>alkyl) ester of the aromatic acid, based on the weight of the reaction mixture.

[0020] In some embodiments, the conversion of aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester to the dialkyl arylate, in particular, the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP, can be greater than 65%, for example, greater than 90%, for example, greater than 95%, for example, greater than 98%, for example, greater than 99%, based on the weight of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester.

[0021] The dialkyl arylate, in particular, the di(C<sub>5-13</sub>alkyl) terephthalate, specifically DOTP, prepared according to the above-described method can be a color of less than 35, for example greater than 0 to less than 35, or 1 to 34, or 5 to 32, or 10 to 32, or 20 to 32, as determined according to ASTM D1209.

[0022] In an embodiment, the above-described process can be particularly useful for the preparation of diisooctyl terephthalate (DOTP). A process for the preparation of diisooctyl terephthalate includes reacting terephthalic acid with 2-ethylhexanol in the presence of an acid catalyst comprising sulfuric acid, a sulfonic acid, or a combination comprising at least one of the foregoing to provide a reaction mixture comprising the diisooctyl terephthalate. In some embodiments, the sulfonic acid is methanesulfonic acid, dodecyl benzene sulfonic acid, para-toluene sulfonic acid, or a combination comprising at least one of the foregoing. The acid catalyst can be present in an amount of 0.2 to 0.5 mole percent, 0.2 to 0.35 mole percent, or 0.22 to 0.33 mole percent, based on the total moles of terephthalic acid. The terephthalic acid and the 2-ethylhexanol can be present in a molar ratio of 1:2.2 to 1:4, or 1:3 to 1:4. The conditions can be as described above.

[0023] The process can further comprise isolating the diisooctyl terephthalate from the reaction mixture, and can be as described above. The process can afford the diisooctyl terephthalate with a selectivity of greater than 95%, for example, greater than 98%, for example, greater than 99%. A selectivity of greater than 95% means that the reaction mixture comprises

the diisooctyl terephthalate and less than 5 wt% of the corresponding mono-octyl terephthalate, based on the weight of the reaction mixture. Similarly, a selectivity of greater than 98% means that the reaction mixture comprises the diisooctyl terephthalate and less than 2 wt% of the corresponding mono-octyl terephthalate, based on the weight of the reaction mixture, and a selectivity of greater than 99% means that the reaction mixture comprises the diisooctyl terephthalate and less than 1 wt% of the corresponding mono-octyl terephthalate, based on the weight of the reaction mixture.

[0024] In some embodiments, the conversion of the terephthalic acid to diisooctyl terephthalate can be greater than 65%, for example, greater than 90%, for example, greater than 95%, for example, greater than 98%, for example, greater than 99%, based on the weight of the terephthalic acid starting material.

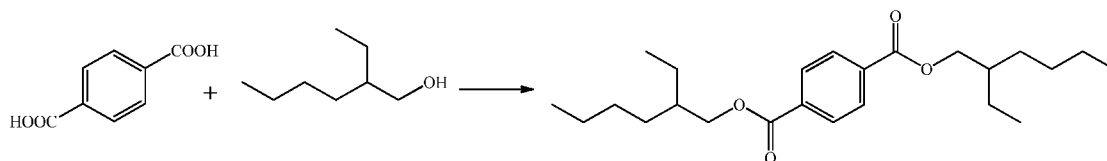
[0025] The diisooctyl terephthalate prepared according to the above-described method can be a color of less than 35, for example greater than 0 to less than 35, or 1 to 34, or 5 to 32, or 10 to 32, or 20 to 32, as determined according to ASTM D1209.

[0026] Further described herein are polymer compositions comprising a polymer and the dialkyl arylates manufactured as described above. The dialkyl arylate can be used as a plasticizer in a variety of polymers, particularly PVC, cellulose acetate-butyrates, cellulose nitrate, polymethyl methacrylate, polystyrene, or polyvinyl butyral. The polymer compositions can be used to manufacture a wide variety of articles, for example beverage closures, sealing materials used in construction joints, and medical devices.

[0027] The processes of the present disclosure are further illustrated by the following examples, which are non-limiting.

## EXAMPLES

[0028] Esterification of terephthalic acid with 2-ethylhexanol was carried out in the presence of methanesulfonic acid (MSA), dodecyl benzene sulfonic acid (DBSA), para-toluene sulfonic acid (PTSA), or sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), according to the chemical reaction shown below.



As a comparison, an esterification reaction was also carried out using a titanium-containing catalyst. The reaction mixture was analyzed using high performance liquid chromatography (HPLC).

[0029] Terephthalic acid (100 grams) and 2-ethylhexanol (3.5 molar equivalents relative to terephthalic acid) were added to a round bottom flask equipped with a mechanical/magnetic stirrer, a Dean-Stark apparatus, and a thermometer for monitoring internal temperature. The flask was placed in an oil bath set to 210°C, and the mixture was heated. The mixture remained as a heterogeneous mixture. The desired catalyst in an amount of 0.22 to 0.33 mole percent was added when the internal temperature reached 170°C. Immediately following catalyst addition, water formation was observed. Water formed during the reaction was collected in the Dean-Stark apparatus. The reactions were carried out for 24 hours. When methanesulfonic acid and sulfuric acid were used as catalysts, a homogenous reaction mixture was observed at 19 hours and 17 hours, respectively. In both of these cases, 100% conversion of terephthalic acid was achieved. In contrast, when a titanium-containing catalyst was used, 90% conversion was achieved after 24 hours.

[0030] The reaction mixture was cooled to less than 100°C. A portion of the 2-ethylhexanol was removed by distillation under vacuum at 7-8 millibar while slowly raising the temperature to 210°C stepwise (130°C, 150°C, 200°C, 210°C). The mixture was then cooled again to 90°C, and 1-3 milliliter of an aqueous alkaline solution (49 wt% sodium hydroxide) was added based on the acid value of the reaction mixture. The mixture was stirred for 30 to 40 minutes and the carbon dioxide gas generated was purged for 20 to 30 minutes. The resulting mixture was further distilled to remove water and the remaining portion of the 2-ethylhexanol using the same distillation method as described previously. Following the second distillation, the mixture was cooled to 120°C and filtered over celite to remove solids. The liquid obtained was then treated with 1 gram of acid-washed activated charcoal, and then filtered over celite to provide pure diisooctyl terephthalate. The selectivity was 99.8%, the color of the diisooctyl terephthalate was 31, determined according to ASTM D1209, and the acid value was 0.04.

[0031] The results obtained for each catalyst test are summarized in Table 1.

Table 1

| Table 1                 |           |           |           |           |                                |                       |
|-------------------------|-----------|-----------|-----------|-----------|--------------------------------|-----------------------|
|                         | Example 1 | Example 2 | Example 3 | Example 4 | Example 5                      | Comparative Example 1 |
| Catalyst                | DBSA      | PTSA      | MSA       | MSA       | H <sub>2</sub> SO <sub>4</sub> | Ti-catalyst           |
| Catalyst Loading (mol%) | 0.22      | 0.22      | 0.22      | 0.33      | 0.33                           | 0.22                  |
| Reaction Time (hours)   | 24        | 24        | 24        | 19        | 17                             | 24                    |
| Conversion of PTA (%)   | 97        | 68        | 98.5      | 100       | 100                            | 90                    |

|                         |    |    |    |      |      |    |
|-------------------------|----|----|----|------|------|----|
| Selectivity to DOTP (%) | 98 | 98 | 98 | 99.8 | 99.5 | 98 |
|-------------------------|----|----|----|------|------|----|

[0032] As demonstrated by Comparative Example 1, when the reaction was carried out using a titanium-containing catalyst, 90% conversion was only achieved after 24 hours, and the reaction mixture remained heterogeneous. Additionally, foaming was a critical problem for this reaction, which significantly hampers the water removal during the reaction. Examples 1 to 3 show that DBSA, PTSA, and MSA catalysts at a loading of 0.22 mole percent provide conversions of 97%, 68%, and 98.5%, respectively. The selectivity for each of these Examples was 98%, and the mixture further included 1 to 1.5% of the corresponding monoester. As shown by Examples 4 and 5, when the catalyst loading was increased to 0.33 mole percent, complete conversion of terephthalic acid was achieved in 19 hours for MSA, and 17 hours for H<sub>2</sub>SO<sub>4</sub>. The selectivity also improved to 99.8% and 99.5% for Examples 4 and 5, respectively.

[0033] The processes described herein are further illustrated by the following embodiments, which are non-limiting.

[0034] Embodiment 1: A process for the preparation of a di(C<sub>5-13</sub>alkyl) arylate comprising reacting an aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof with a C<sub>5-13</sub> alcohol in the presence of an acid catalyst comprising sulfuric acid, a sulfonic acid, or a combination comprising at least one of the foregoing, to provide a reaction mixture comprising the di(C<sub>5-13</sub>alkyl) arylate; wherein the acid catalyst is present in an amount of 0.1 to 0.5 mole percent, based on the moles of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof; and the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof and the C<sub>5-13</sub> alcohol are present in a molar ratio of at least 1:2.2.

[0035] Embodiment 2: The process of embodiment 1, further comprising isolating the di(C<sub>5-13</sub>alkyl) arylate from the reaction mixture, wherein isolating the di(C<sub>5-13</sub>alkyl) arylate comprises: distilling the reaction mixture to remove at least a portion of the residual C<sub>5-13</sub> alcohol from the reaction mixture and neutralizing the acid catalyst to provide a first intermediate mixture; distilling the first intermediate mixture to remove water and a final portion of the residual C<sub>5-13</sub> alcohol to provide a second intermediate mixture; and filtering the second intermediate mixture to provide a filtrate comprising the di(C<sub>5-13</sub>alkyl) arylate.

[0036] Embodiment 3: The process of embodiment 2, wherein isolating the di(C<sub>5-13</sub>alkyl) arylate further comprises: treating the filtrate with activated charcoal; and filtering the treated mixture to provide the di(C<sub>5-13</sub>alkyl) arylate.

[0037] Embodiment 4: The process of any of embodiments 1 to 3, wherein the di(C<sub>5-13</sub>alkyl) arylate is a di(C<sub>5-13</sub>alkyl) terephthalate, and the aromatic acid is terephthalic acid;

preferably wherein the di(C<sub>5-13</sub>alkyl) arylate is a diisooctyl terephthalate, the C<sub>5-13</sub> alcohol is isooctyl alcohol, and the aromatic acid is terephthalic acid.

[0038] Embodiment 5: The process of any of embodiments 1 to 4, wherein the sulfonic acid is methanesulfonic acid, dodecyl benzene sulfonic acid, para-toluene sulfonic acid, or a combination comprising at least one of the foregoing.

[0039] Embodiment 6: The process of any of embodiments 1 to 5, wherein the reaction mixture comprises the di(C<sub>5-13</sub>alkyl) arylate and less than 5 wt%, preferably less than 2 wt%, more preferably less than 1 wt% of the corresponding mono(C<sub>5-13</sub>alkyl) ester of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester, based on the weight of the reaction mixture.

[0040] Embodiment 7: The process of any of embodiments 1 to 6, wherein conversion of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester is greater than 65%, preferably greater than 90%, more preferably greater than 95%, even more preferably greater than 98%, even more preferably greater than 99%, based on the weight of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester.

[0041] Embodiment 8: The process of any of embodiments 1 to 7, wherein the di(C<sub>5-13</sub>alkyl) arylate has a color of less than 35, determined according to ASTM D1209.

[0042] Embodiment 9: The process of any of embodiments 1 to 8, wherein the C<sub>5-13</sub> alcohol comprises hexanol, cyclohexanol, heptanol, 2-ethylhexanol, cyclohexanemethanol, methylcyclohexanemethanol, octanol, nonanol, decanol, 2-propylheptanol, benzyl alcohol, 2-phenyl ethanol, or a combination comprising at least one of the foregoing.

[0043] Embodiment 10: The process of any of embodiments 1 to 9, wherein the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester and the C<sub>5-13</sub> alcohol are present in a molar ratio of at least 1:3, preferably at least 1:3.5.

[0044] Embodiment 11: The process of any of embodiments 1 to 10, wherein the acid catalyst is present in an amount of 0.2 to 0.5 mole percent, preferably 0.22 to 0.33 mole percent, based on the moles of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester.

[0045] Embodiment 12: The process of any of embodiments 1 to 11, wherein the acid catalyst comprises sulfuric acid, methanesulfonic acid, or a combination comprising at least one of the foregoing.

[0046] Embodiment 13: The process of any of embodiments 1 to 12, wherein the acid catalyst is sulfuric acid, methanesulfonic acid, or a combination comprising at least one of the foregoing and is present in an amount of 0.22 to 0.33 mole percent, based on the total moles of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester.

[0047] Embodiment 14: The process of any of embodiments 1 to 13, wherein the reacting is at a temperature of 180 to 230°C and a pressure of 0.3 to 2 bar.

[0048] Embodiment 15: The process of any of embodiments 1 to 14, wherein the reacting is for a period of 12 to 24 hours.

[0049] Embodiment 16: The process of any of embodiments 1 to 15, wherein the reaction mixture further comprises residual C<sub>5-13</sub> alcohol, water, a C<sub>1-3</sub> alcohol, or a combination comprising at least one of the foregoing.

[0050] Embodiment 17: The process of any of embodiments 1 to 16, wherein the reaction mixture is a homogenous mixture when conversion of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester is greater than 95%.

[0051] Embodiment 18: A process for the preparation of diisooctyl terephthalate comprising reacting terephthalic acid with 2-ethylhexanol in the presence of an acid catalyst comprising sulfuric acid, a sulfonic acid, or a combination comprising at least one of the foregoing to provide a reaction mixture comprising the diisooctyl terephthalate; wherein the acid catalyst is present in an amount of 0.2 to 0.5 mole percent, based on the moles of the terephthalic acid; and the terephthalic acid and the 2-ethylhexanol are present in a molar ratio of 1:2.2 to 1:4.

[0052] Embodiment 19: The process of embodiment 18, further comprising isolating the diisooctyl terephthalate from the reaction mixture, wherein isolating the diisooctyl terephthalate comprises: distilling the reaction mixture to remove at least a portion of the residual 2-ethylhexanol from the reaction mixture and neutralizing the acid catalyst to provide a first intermediate mixture; distilling the first intermediate mixture to remove water and a final portion of the residual 2-ethylhexanol to provide a second intermediate mixture; and filtering the second intermediate mixture to provide a filtrate comprising the diisooctyl terephthalate.

[0053] Embodiment 20: The process of embodiment 19, wherein isolating the diisooctyl terephthalate further comprises: treating the filtrate with activated charcoal; and filtering the treated filtrate to provide the diisooctyl terephthalate.

[0054] Embodiment 21: The process of any of embodiments 19 to 20, wherein the sulfonic acid is methanesulfonic acid, dodecyl benzene sulfonic acid, para-toluene sulfonic acid, or a combination comprising at least one of the foregoing.

[0055] Embodiment 22: The process of any of embodiments 19 to 21, wherein the reaction mixture comprises the diisooctyl terephthalate and less than 5 wt%, preferably less than 2wt%, more preferably less than 1wt% of the corresponding monoalkyl ester of the terephthalic acid, based on the weight of the reaction mixture.

[0056] Embodiment 23: The process of any of embodiments 19 to 22, wherein conversion of the terephthalic acid is greater than 65%, preferably greater than 90%, more preferably greater than 95%, even more preferably greater than 98%, even more preferably greater than 99%, based on the weight of the terephthalic acid.

[0057] Embodiment 24: The process of any of embodiments 19 to 23, wherein the diisooctyl terephthalate has a color of less than 35, determined according to ASTM D1209.

[0058] Embodiment 25: The process of any of embodiments 19 to 24, wherein the acid catalyst is sulfuric acid, methanesulfonic acid, or a combination comprising at least one of the foregoing and is present in an amount of 0.22 to 0.33 mole percent, based on the total moles of the terephthalic acid.

[0059] Embodiment 26: The process of any of embodiments 19 to 25, wherein the reaction mixture is homogenous when conversion of the terephthalic acid is greater than 95%.

[0060] The processes can alternatively comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The processes can additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants, species or process steps used in the prior art compositions or processes or that are otherwise not necessary to the achievement of the function and/or objectives of the present invention. The endpoints of all ranges directed to the same component or property are inclusive and independently combinable. Disclosure of a narrower range or more specific group in addition to a broader range is not a disclaimer of the broader range or larger group.

“Combination” is inclusive of blends, mixtures, alloys, reaction products, and the like.

Furthermore, the terms “first,” “second,” and the like, herein do not denote any order, quantity, or importance, but rather are used to denote one element from another. The terms “a” and “an” and “the” herein do not denote a limitation of quantity, and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context.

“Or” means “and/or.” The suffix “(s)” as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including one or more of that term. Reference throughout the specification to “an embodiment”, “another embodiment”, “some embodiments”, and so forth, means that a particular element described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments. “Optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event occurs and instances where it does not. Unless defined

otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs.

[0061] Unless otherwise specified herein, any reference to standards, regulations, testing methods and the like, such as ASTM D1209 refer to the standard, regulation, guidance or method that is in force at the time of filing of the present application.

[0062] All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

[0063] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

## CLAIMS:

What is claimed is:

1. A process for the preparation of a di(C<sub>5-13</sub>alkyl) arylate, comprising:  
reacting an aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof with a C<sub>5-13</sub> alcohol in the presence of an acid catalyst comprising sulfuric acid, a sulfonic acid, or a combination comprising at least one of the foregoing, to provide a reaction mixture comprising the di(C<sub>5-13</sub>alkyl) arylate;  
wherein  
the acid catalyst is present in an amount of 0.1 to 0.5 mole percent, based on the moles of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof; and  
the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof and the C<sub>5-13</sub> alcohol are present in a molar ratio of at least 1:2.2.
2. The process of Claim 1, further comprising isolating the di(C<sub>5-13</sub>alkyl) arylate from the reaction mixture, wherein isolating the di(C<sub>5-13</sub>alkyl) arylate comprises:  
distilling the reaction mixture to remove at least a portion of the residual C<sub>5-13</sub> alcohol from the reaction mixture and neutralizing the acid catalyst to provide a first intermediate mixture;  
distilling the first intermediate mixture to remove water and a final portion of the residual C<sub>5-13</sub> alcohol to provide a second intermediate mixture; and  
filtering the second intermediate mixture to provide a filtrate comprising the di(C<sub>5-13</sub>alkyl) arylate.
3. The process of Claim 2, wherein isolating the di(C<sub>5-13</sub>alkyl) arylate further comprises:  
treating the filtrate with activated charcoal; and  
filtering the treated mixture to provide the di(C<sub>5-13</sub>alkyl) arylate.
4. The process of any of Claims 1 to 3,  
wherein the di(C<sub>5-13</sub>alkyl) arylate is a di(C<sub>5-13</sub>alkyl) terephthalate, and the aromatic acid is terephthalic acid, preferably wherein the di(C<sub>5-13</sub>alkyl) arylate is a diisooctyl terephthalate, the C<sub>5-13</sub> alcohol is isooctyl alcohol, and the aromatic acid is terephthalic acid.

5. The process of any of Claims 1 to 4, wherein the sulfonic acid is methanesulfonic acid, dodecyl benzene sulfonic acid, para-toluene sulfonic acid, or a combination comprising at least one of the foregoing.

6. The process of any of Claims 1 to 5, wherein the reaction mixture comprises the di(C<sub>5-13</sub>alkyl) arylate and less than 5 wt%, preferably less than 2 wt%, more preferably less than 1 wt% of the corresponding mono(C<sub>5-13</sub>alkyl) ester of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester, based on the weight of the reaction mixture.

7. The process of any of Claims 1 to 6, wherein conversion of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof is greater than 65%, preferably greater than 90%, more preferably greater than 95%, even more preferably greater than 98%, even more preferably greater than 99%, based on the weight of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester.

8. The process of any of Claims 1 to 7, wherein the di(C<sub>5-13</sub>alkyl) arylate has a color of less than 35, determined according to ASTM D1209.

9. The process of any of Claims 1 to 8, wherein the C<sub>5-13</sub> alcohol comprises hexanol, cyclohexanol, heptanol, 2-ethylhexanol, cyclohexanemethanol, methylcyclohexanemethanol, octanol, nonanol, decanol, 2-propylheptanol, benzyl alcohol, 2-phenyl ethanol, or a combination comprising at least one of the foregoing.

10. The process of any of Claims 1 to 9, wherein the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester and the C<sub>5-13</sub> alcohol are present in a molar ratio of at least 1:3, preferably at least 1:3.5.

11. The process of any of Claims 1 to 10, wherein the acid catalyst is present in an amount of 0.2 to 0.5 mole percent, preferably 0.22 to 0.33 mole percent, based on the moles of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof.

12. The process of any of Claims 1 to 11, wherein the acid catalyst comprises sulfuric acid, methanesulfonic acid, or a combination comprising at least one of the foregoing, preferably wherein the acid catalyst is sulfuric acid, methanesulfonic acid, or a combination comprising at

least one of the foregoing and is present in an amount of 0.22 to 0.33 mole percent, based on the total moles of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof.

13. The process of any of Claims 1 to 12, wherein the reacting is at a temperature of 180 to 230°C and a pressure of 0.3 to 2 bar for a period of 12 to 24 hours.

14. The process of any of Claims 1 to 13, wherein the reaction mixture is a homogenous mixture when conversion of the aromatic acid, anhydride, or di(C<sub>1-3</sub>alkyl)ester thereof is greater than 95%.

15. A process for the preparation of diisooctyl terephthalate, comprising:  
reacting terephthalic acid with 2-ethylhexanol in the presence of an acid catalyst comprising sulfuric acid, a sulfonic acid, or a combination comprising at least one of the foregoing to provide a reaction mixture comprising the diisooctyl terephthalate;

wherein

the acid catalyst is present in an amount of 0.2 to 0.5 mole percent, based on the moles of the terephthalic acid; and

the terephthalic acid and the 2-ethylhexanol are present in a molar ratio of 1:2.2 to 1:4.

16. The process of Claim 15, further comprising isolating the diisooctyl terephthalate from the reaction mixture, wherein isolating the diisooctyl terephthalate comprises:

distilling the reaction mixture to remove at least a portion of the residual 2-ethylhexanol from the reaction mixture and neutralizing the acid catalyst to provide a first intermediate mixture;

distilling the first intermediate mixture to remove water and a final portion of the residual 2-ethylhexanol to provide a second intermediate mixture; and

filtering the second intermediate mixture to provide a filtrate comprising the diisooctyl terephthalate.

17. The process of Claim 16, wherein isolating the diisooctyl terephthalate further comprises:

treating the filtrate with activated charcoal; and

filtering the treated filtrate to provide the diisooctyl terephthalate.

18. The process of any of Claims 15 to 17, wherein the reaction mixture comprises the diisooctyl terephthalate and less than 5 wt%, preferably less than 2wt%, more preferably less than 1wt% of the corresponding monoalkyl ester of the terephthalic acid, based on the weight of the reaction mixture.

19. The process of any of claims 15 to 18, wherein conversion of the terephthalic acid is greater than 65%, preferably greater than 90%, more preferably greater than 95%, even more preferably greater than 98%, even more preferably greater than 99%, based on the weight of the terephthalic acid.

20. The process of any of claims 15 to 19, wherein the diisooctyl terephthalate has a color of less than 35, determined according to ASTM D1209 and wherein the reaction mixture is homogenous when conversion of the terephthalic acid is greater than 95%.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2016/057939

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C07C67/08 C07C69/80 C07C69/82  
ADD.

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)  
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 practicable, search terms used)

EP0-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages         | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------|-----------------------|
| X         | FR 2 974 084 A1 (ARKEMA FRANCE [FR])<br>19 October 2012 (2012-10-19)                       | 1-14                  |
| Y         | examples 1,3                                                                               | 15-20                 |
| Y         | -----<br>WO 2015/063189 A1 (BASF SE [DE])<br>7 May 2015 (2015-05-07)<br>example 1<br>----- | 15-20                 |

☐

Further documents are listed in the continuation of Box C.

☒

See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

2 March 2017

Date of mailing of the international search report

09/03/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

de Nooy, Arjan

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2016/057939

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|----|---------------------|----------------------------|---------------------|
| FR 2974084                                | A1 | 19-10-2012          | NONE                       |                     |
| -----                                     |    |                     |                            |                     |
| WO 2015063189                             | A1 | 07-05-2015          | CA 2926388 A1              | 07-05-2015          |
|                                           |    |                     | CN 105683147 A             | 15-06-2016          |
|                                           |    |                     | EP 3063122 A1              | 07-09-2016          |
|                                           |    |                     | JP 2016536313 A            | 24-11-2016          |
|                                           |    |                     | KR 20160079065 A           | 05-07-2016          |
|                                           |    |                     | US 2016264509 A1           | 15-09-2016          |
|                                           |    |                     | WO 2015063189 A1           | 07-05-2015          |
| -----                                     |    |                     |                            |                     |