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(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 560 052 (IN). MANCHANA,

Ravinath; Plot No. 81 to 85 Village: Chikkadunnasandra,

Anekal: Taluk, off Sarjapura - Attibele State Highway, Ban-

galore 562 125, Karnataka (IN). NAIR, Vinod Sankaran;

Plot No. 81 to 85 Village: Chikkadunnasandra, Anekal:

Taluk, off Sarjapura - Attibele State Highway, Bangalore

5621 25, Karnataka (IN). DESHPANDE, Hareesh Sham-

rao; Plot No. 81 to 85 Village: Chikkadunnasandra, Anekal:

Taluk, off Sarjapura - Attibele State Highway, Bangalore

562 125, Karnataka (IN).

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(54) Title: METHODS OF MANUFACTURE OF TRIALKYL TRICARBOXYLATES, AND TRIALKYL TRICARBOXYLATES MADE BY THE METHODS

(57) Abstract: A method of making trialkyl tricarboxylates includes melting a phenyl tricarboxylic acid or anhydride thereof to provide a molten phenyl tricarboxylic acid or anhydride thereof; combining the molten phenyl tricarboxylic acid or anhydride thereof and greater than 3.0 molar equivalents of a C₄₋₁₈ alkyl alcohol, for example, greater than 3.5 molar equivalents of a C₄₋₁₈ alkyl alcohol, based on the total moles of phenyl tricarboxylic acid or an anhydride thereof, to provide a melt mixture; adding 0.05 mol% to 0.20 mol% of a titanium tetraalkoxide catalyst, based on the total moles of phenyl tricarboxylic acid or anhydride thereof, to the melt mixture to form a reaction mixture; reacting the phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol in the reaction mixture to form a product mixture having an acid value equal to or less than 0.5, as determined according to ASTM D1045, and including the trialkyl tricarboxylate; and isolating the trialkyl tricarboxylate from the product mixture.



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METHODS OF MANUFACTURE OF TRIALKYL TRICARBOXYLATES, AND TRIALKYL TRICARBOXYLATES MADE BY THE METHODS

BACKGROUND

[0001] Plasticizers are widely used in many polymer compositions, including coating compositions, sealing compositions, and rubber compositions. Dioctyl phthalate (DOP) and trialkyl tricarboxylate are examples of such plasticizers. Alternative methods for the manufacture of trialkyl tricarboxylates would be useful in the art.

BRIEF DESCRIPTION

[0002] A method of making trialkyl tricarboxylates includes melting a phenyl tricarboxylic acid or anhydride thereof to provide a molten phenyl tricarboxylic acid or anhydride thereof; combining the molten phenyl tricarboxylic acid or anhydride thereof and greater than 3.0 molar equivalents of a C₄₋₁₈ alkyl alcohol, for example, greater than 3.0 molar equivalents of a C₄₋₁₈ alkyl alcohol, based on the total moles of phenyl tricarboxylic acid or anhydride thereof, to provide a melt mixture; adding 0.05 mole percent (mol%) to 0.20 mol% of a titanium tetraalkoxide catalyst, based on the total moles of phenyl tricarboxylic acid or anhydride thereof, to the melt mixture to form a reaction mixture; reacting the phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol in the reaction mixture to form a product mixture having an acid value equal to or less than 0.5, preferably equal to or less than 0.3, more preferably equal to or less than 0.2, as determined according to ASTM D1045, and including the trialkyl tricarboxylate; and isolating the trialkyl tricarboxylate from the product mixture.

[0003] A method for sequential manufacture of trialkyl tricarboxylate and dioctyl phthalate in a reactor includes manufacturing the trialkyl tricarboxylate in the reactor. Manufacturing the trialkyl tricarboxylate includes melting a phenyl tricarboxylic acid or anhydride thereof to provide a molten phenyl tricarboxylic acid or anhydride thereof, combining the molten phenyl tricarboxylic acid or anhydride thereof and a C₄₋₁₈ alkyl alcohol to provide a melt mixture, adding a titanium tetraalkoxide catalyst to the melt mixture to form a reaction mixture, and reacting the phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol in the reaction mixture to form a product mixture including the trialkyl tricarboxylate. The method further includes manufacturing the dioctyl phthalate in the reactor. Manufacturing the dioctyl phthalate includes reacting a phthalic anhydride with a C₄₋₁₈ alkyl alcohol in the presence of a homogeneous catalyst in a reactor to form a phthalate product mixture. The

method also includes removing the product mixture comprising the trialkyl tricarboxylate from the reactor prior to manufacturing the dioctyl phthalate in the reactor or removing the phthalate product mixture from the reactor prior to manufacturing the trialkyl tricarboxylate in the reactor.

[0004] A method for the manufacture of trialkyl tricarboxylate includes melting a trimellitic anhydride to provide a molten trimellitic anhydride; combining the molten trimellitic anhydride and greater than 3.0 molar equivalents of 2-ethylhexyl alcohol, for example, greater than 3.5 molar equivalents of 2-ethylhexyl alcohol, based on the total moles of trimellitic anhydride, to provide a melt mixture; adding 0.05 mol% to 0.20 mol% of titanium tetra-isopropoxide catalyst, based on the total moles of trimellitic anhydride, to the melt mixture to form a reaction mixture; reacting the trimellitic anhydride and the 2-ethylhexyl alcohol in the reaction mixture to form a product mixture having an acid value equal to or less than 0.5, preferably equal to or less than 0.3, more preferably equal to or less than 0.2, as determined according to ASTM D1045, and including the trialkyl tricarboxylate; and isolating the trialkyl tricarboxylate from the product mixture.

[0005] Also described is the trialkyl tricarboxylate made by any of the foregoing methods, as well as a polymer composition comprising the trialkyl tricarboxylate made by any of the foregoing methods.

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

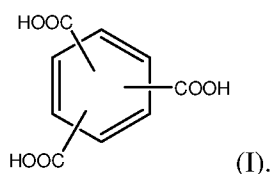
DETAILED DESCRIPTION

[0007] Trialkyl tricarboxylate offers an alternative to dioctyl phthalate (DOP) plasticizers. By making trialkyl tricarboxylates in a manner similar to the method for making DOP, both types of plasticizers can be made in the same facility or the facility can be readily converted to the manufacture of trialkyl tricarboxylates. This provides greater flexibility and efficiency in the manufacturing process of both compounds.

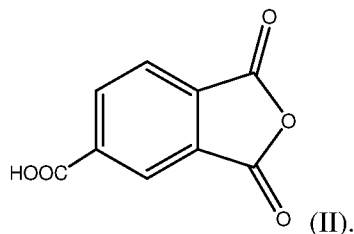
[0008] As described above, a method of making trialkyl tricarboxylates includes melting a phenyl tricarboxylic acid or an anhydride of a phenyl tricarboxylic acid. The molten compound is then combined with a C₄₋₁₈ alkyl alcohol to provide a melt mixture. Greater than 3.0 molar equivalents of the C₄₋₁₈ alkyl alcohol, for example, greater than 3.5 molar equivalents of the C₄₋₁₈ alkyl alcohol, based on the total moles of phenyl tricarboxylic acid or anhydride is used. Next, a titanium tetraalkoxide catalyst is added to the melt mixture to provide a reaction mixture. The amount of titanium tetraalkoxide catalyst is 0.05 mol% to 0.20 mol%, based on the total moles of phenyl tricarboxylic acid or anhydride. Reacting the phenyl tricarboxylic acid or

anhydride and the C₄₋₁₈ alkyl alcohol in the reaction mixture forms a product mixture that includes the trialkyl tricarboxylate. The product mixture has an acid value of 0.5 or less, preferably 0.3 or less, more preferably 0.2 or less. The acid value can be determined according to ASTM D1045. The trialkyl tricarboxylate can then be isolated from the product mixture.

[0009] The phenyl tricarboxylic acid has the Formula (I):



In some embodiments the phenyl tricarboxylic acid includes compounds in which two of the carboxylic acid groups are located at adjacent carbons and together form an anhydride. An exemplary anhydride is trimellitic anhydride (TMA) as shown in Formula (II):



The anhydride of any such phenyl tricarboxylic acid can be used instead of, or in combination with, the tricarboxylic acid. Accordingly, any combination of a phenyl tricarboxylic acid and an anhydride of a tricarboxylic acid can be used. In particular, a combination of more than one type of phenyl tricarboxylic acid or more than one type of dianhydride of a phenyl tricarboxylic acid can be used; a combination of one or more phenyl tricarboxylic acid and the corresponding one or more anhydrides can be used; or one or more phenyl tricarboxylic acids and one or more dianhydrides of different tricarboxylic acids can be used. For convenience herein “phenyl tricarboxylic acid or anhydride thereof” is intended to encompass a phenyl tricarboxylic acid alone, an anhydride of a tricarboxylic acid alone, or any of the foregoing combinations. In some embodiments the dianhydride is TMA.

[0010] The phenyl tricarboxylic acid or anhydride thereof is melted to provide a molten phenyl tricarboxylic acid or anhydride thereof. Advantageously, molten phenyl tricarboxylic acid or anhydride thereof can provide an improvement in the handling of the phenyl tricarboxylic acid or anhydride thereof relative to use of solid phenyl tricarboxylic acid or anhydride thereof. Melting of the phenyl tricarboxylic acid or anhydride thereof can be conducted at a temperature above the melting point of the phenyl tricarboxylic acid or anhydride

thereof. In some embodiments the melting is conducted at 165°C or greater, for example, 165°C to 190°C, 165°C to 180°C, or 165°C to 170°C.

[0011] The C₄₋₁₈ alkyl alcohol is saturated, unsubstituted and can be straight chain or branched. Exemplary alcohols include n-butanol, octanol, iso-nonanol, isodecanol, decanol, and 2-ethylhexyl alcohol. In some embodiments the C₄₋₁₈ alkyl alcohol includes 2-ethylhexyl alcohol. The C₄₋₁₈ alkyl alcohol is present in the reaction in an amount greater than or equal to 3.0 molar equivalents, for example, greater than or equal to 3.5 molar equivalents, based on the amount of the phenyl tricarboxylic acid or chemical equivalent thereof. In some embodiments the C₄₋₁₈ alkyl alcohol is present in an amount in a range of 3.0 molar equivalents to 4.5 molar equivalents, or, more specifically, 3.0 molar equivalents to 4.0 molar equivalents or 3.5 molar equivalents to 4.0 molar equivalents. Advantageously, use of the molten phenyl tricarboxylic acid or anhydride thereof can provide an improvement in control of a molar ratio of the phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl, relative to use of solid phenyl tricarboxylic acid or anhydride thereof. In some embodiments, the anhydride is TMA and the alcohol is 2-ethylhexyl alcohol.

[0012] The C₄₋₁₈ alkyl alcohol can be heated to a temperature in a range of 80°C to 140°C, preferably 90°C to 130°C, more preferably 100°C to 120°C, prior to combining the molten phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol.

[0013] Suitable homogeneous catalysts that can be used include acids, such as sulfuric acid, methanesulfonic acid, or p-toluenesulfonic acid, or metal compounds. Examples of relevant metals include tin, titanium, and zirconium in the form of their salts, oxides, or soluble organic compounds. Exemplary representatives of metal catalysts include (C₁₋₈ alkyl) zirconates such as tetrabutyl zirconate. Preferred catalysts are the titanium tetraalkoxide catalysts including four alkoxide ligands, each having 1 to 18 carbons, preferably 1 to 8 carbon atoms. It is contemplated that the titanium tetraalkoxide can include a mixture of alkoxide ligands having a different number of carbons, the four alkoxide ligands can all have the same number of carbons but be different isomers, or the four alkoxide ligands can have the same number of carbons and the same structure. Exemplary titanium tetraalkoxide catalysts include titanium tetra-isopropoxide, titanium tetra-butoxide, or a combination thereof.

[0014] The catalyst concentration can be varied in wide ranges and in particular can be varied as a function of the type of catalyst. The titanium tetraalkoxide can be present in an amount in a range of 0.05 mole percent (mol%) to 0.20 mol% or 0.11 mol% to 0.16 mol%, based on the total moles phenyl tricarboxylic acid or anhydride thereof.

[0015] A temperature of the reaction of the phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol can be at any temperature effective to conduct the reaction in an efficient amount of time, and that preferably minimizes energy use or byproducts. For example, the temperature of the reaction can be in a range of 150°C to 230°C, for example, in a range of 170°C to 230°C. Within this range, the temperature can be in a range of 200°C to 220°C or 210°C to 215°C. Similarly, any suitable pressure can be used, for example atmospheric pressure.

[0016] The time for the reaction can advantageously be less equal to or than 7 hours. Within this range, the time for the reaction can be equal to or less than 6.5 hours or equal or less than 6 hours. When the reaction mixture has an acid value less than 0.5 as determined according to ASTM D1045 the reaction can be deemed complete.

[0017] Advantageously, use of molten phenyl tricarboxylic acid or anhydride thereof can provide improved reaction rates, and a corresponding cycle time can be reduced, relative to use of solid phenyl tricarboxylic acid or anhydride thereof. Use of molten phenyl tricarboxylic acid or anhydride thereof can provide improved reaction rates at lower temperatures, relative to use of solid phenyl tricarboxylic acid or anhydride thereof. Faster reaction rates can result in lesser amounts impurities in the product trialkyl tricarboxylate. For example, a purity of the trialkyl tricarboxylate is equal to or greater than 98.0 weight percent (wt.%), preferably equal to or greater than 98.5 wt.%, more preferably equal to or greater than 99.0 wt.%, based on the total weight of the trialkyl tricarboxylate, can be achieved.

[0018] After the reaction is complete the product trialkyl tricarboxylate can be isolated from the remainder of the reaction mixture. Isolation includes removal of the excess C₄₋₁₈ alkyl alcohol. The excess C₄₋₁₈ alkyl alcohol can be removed by distillation under reduced pressure. For example, when the alcohol is 2-ethylhexyl alcohol distillation can occur at a temperature in a range of 135°C to 230°C and a pressure in a range of 7 millibars to 20 millibars, for example, 7 millibars to 8 millibars.

[0019] After removal of the excess C₄₋₁₈ alkyl alcohol the temperature of the distilled mixture can be reduced to less than 100°C and an aqueous base solution can be introduced to neutralize the reaction mixture. It is also contemplated that the reaction mixture can be neutralized prior to removal of any excess C₄₋₁₈ alkyl alcohol. The aqueous base solution can include a base such as sodium hydroxide, potassium hydroxide, calcium oxide, or the like. The amount of aqueous base solution added to the reaction mixture is selected to provide an amount of base which is equivalent to or a slight excess to the amount of acid in the reaction mixture. Exemplary amounts are in a range of 1 wt.% to 3 wt.%, based on the weight of phenyl

tricarboxylic acid or dianhydride added to the reaction, of a basic solution having a concentration in a range of about 40 wt.% base to 60 wt.% base, based on the total weight of the basic solution. Neutralization can proceed for a period of time in a range, for example, of 30 minutes to 40 minutes and the neutralized mixture can become milky or cloudy.

[0020] The neutralized reaction mixture can be treated to remove excess base, for example purged with carbon dioxide to neutralize excess base. Purging can occur over a time period of time, for example in a range of 10 minutes to 60 minutes, 15 minutes to 45 minutes, or, more specifically, 20 minutes to 30 minutes. The purged mixture can be distilled to remove water, for example at a temperature in a range of 40°C to 70°C, for example, 40°C to 50°C, and at a reduced pressure such as in a range of 7 millibars to 20 millibars, for example, 7 millibars to 8 millibars. After the water is removed the temperature of the mixture can be increased to remove any residual C₄₋₁₈ alkyl alcohol while maintaining the mixture at a reduced pressure. The mixture can then be cooled to a temperature, for example in a range of 90°C to 140°C, or more specifically, 90°C to 120°C, 100°C to 120°C, or 100 to 110 °C and filtered to remove particulates, for example through diatomaceous earth, Fuller's earth, perlite, other filter medium, or combination thereof. Alternatively, the mixture can be centrifuged or otherwise treated to remove particulates.

[0021] The filtered liquid can be further purified, for example decolorized. For example, the filtered liquid can be treated with a decolorizing agent such as charcoal for a period of time in a range of 25 minutes to 45 minutes or 30 minutes to 40 minutes at a temperature in a range of 50°C to 70°C, or 55°C to 65°C. After the charcoal treatment the charcoal is removed, for example the mixture can be centrifuged or filtered over a filter medium such as celite. It is advantageous to conduct any filtration at a temperature in a range of 60°C to 100°C, for example, 90°C to 110°C, due to the viscosity of the product. The amount of celite and charcoal used in the foregoing isolation steps can be in range of 0.5 wt.% to 2 wt.%, based on the weight of the phenyl tricarboxylic acid or anhydride thereof used in the reaction.

[0022] The final trialkyl tricarboxylate product can have an acid value less than or equal to 0.1 as determined by ASTM D1045, or an APHA color value less than 30 as determined by ASTM 1290, or both. In an embodiment, the trialkyl tricarboxylate is a tri(2-ethylhexyl) trimellitate (TOTM). The tri(2-ethylhexyl) trimellitate can have an acid value less than or equal to 0.1 as determined by ASTM D1045, or an APHA color value less than 30 as determined by ASTM 1290, or both.

[0023] As above, this method for manufacture of trialkyl tricarboxylates can advantageously be conducted in the same facility and using the same equipment, as the

manufacture of dioctyl phthalate. Methods for the melt manufacture of dioctyl phthalate are known, being described for example, in WO 2007/021475 or WO 2013/143824. The same or similar catalysts and conditions as described above can be used. In some embodiments, the method includes reacting a phthalic anhydride with a C₄₋₁₈ alkyl alcohol in the presence of a homogeneous catalyst in a reactor to form a phthalate product mixture. Suitable reactors are known, for example a batch reactor, a continuous flow reactor, such as a distillation column and/or tower, or a cascade of stirred tank reactors. Manufacture of the trialkyl tricarboxylates and the dioctyl phthalate can be carried out batch-wise or continuously. Preferably the sequential manufacturing is carried out batch-wise.

[0024] Accordingly, a method for sequential manufacture of trialkyl tricarboxylate and dioctyl phthalate includes manufacturing trialkyl tricarboxylate and manufacturing dioctyl phthalate sequentially in the same reactor. The trialkyl tricarboxylate can be manufactured (as described above) prior to the dioctyl phthalate or the dioctyl phthalate can be manufactured prior to the trialkyl tricarboxylate. When the trialkyl tricarboxylate is manufactured prior to the dioctyl phthalate, the method includes removing the product mixture comprising the trialkyl tricarboxylate from the reactor prior to manufacturing the dioctyl phthalate in the reactor. When the dioctyl phthalate is manufactured prior to the trialkyl tricarboxylate, the method also includes removing the phthalate product mixture from the reactor prior to manufacturing the trialkyl tricarboxylate in the reactor.

[0025] Stated otherwise, as the process for the manufacture of trialkyl tricarboxylate that can take advantage of current commercial infrastructure for the manufacture of DOP, a method for sequential manufacture of trialkyl tricarboxylate and dioctyl phthalate includes performing a first portion of the method using a reactor, the first portion of the method including manufacturing the trialkyl tricarboxylate or manufacturing the dioctyl phthalate; removing a reaction product of the first portion of the method from the reactor; and performing a second portion of the method using the reactor, the second portion of the method including the other of manufacturing the trialkyl tricarboxylate or manufacturing the dioctyl phthalate not performed in the first portion of the method. Manufacturing the trialkyl tricarboxylate includes melting a phenyl tricarboxylic acid or anhydride thereof to provide a molten phenyl tricarboxylic acid or anhydride thereof, combining the molten phenyl tricarboxylic acid or anhydride thereof and a C₄₋₁₈ alkyl alcohol to provide a melt mixture, adding a titanium tetraalkoxide catalyst to the melt mixture to form a reaction mixture, and reacting the phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol in the reaction mixture to form a product mixture including the trialkyl tricarboxylate. Manufacturing the dioctyl phthalate includes reacting a phthalic

anhydride with a C₄₋₁₈ alkyl alcohol in the presence of a homogeneous catalyst in a reactor to form a phthalate product mixture.

[0026] Additionally, dioctyl terephthalate can be manufactured using the same reactor. For example, dioctyl terephthalate can be sequentially manufactured prior to manufacturing the trialkyl tricarboxylate and the dioctyl phthalate, after manufacturing the trialkyl tricarboxylate and the dioctyl phthalate, prior to manufacturing the trialkyl tricarboxylate and after manufacturing the dioctyl phthalate, or prior to manufacturing the dioctyl phthalate and after manufacturing the trialkyl tricarboxylate.

[0027] The trialkyl tricarboxylates manufactured by the methods described herein can be used in any application, in particular in combination with another polymer. A polymer composition accordingly comprises the trialkyl tricarboxylate and a polymer. A wide variety of thermoplastic or thermosetting polymers can be used, for example a polymer or copolymer of vinyl chloride, preferably a homopolymer of polyvinyl chloride (PVC), a polyolefin such as a polypropylene or a copolymer thereof, a polyethylene or a copolymer thereof, a polyvinyl acetate or a copolymer thereof, a poly(meth)acrylic or copolymer thereof, a poly(C₁₋₈ alkyl)(meth)acrylate, a cellulosic thermoplastic, a polyamide, a polyimide, a polycarbonate, a polysulfide, a polyurethane, a polyvinylbutyral, a polyvinylbutyral-polyvinylalcohol copolymer, a synthetic rubber such as butadiene-acrylonitrile, butadiene-styrene, styrene-butadiene-styrene, or a chloroprene rubber, a polyester, a phenolic resin, a urea formaldehyde resin, or a melamine resin. A combination of different polymers can be used, such as polypropylene blended with and/or grafted to an ethylene/propylene rubbery substrate. The polymer composition can contain other additives such as stabilizers, fillers, pigments, foaming agents, or other conventional additives. The amount of the trialkyl tricarboxylate can vary widely as is known in the art, depending on its function, for example plasticization or other function.

[0028] This disclosure is further illustrated by the following example, which is non-limiting.

EXAMPLE

[0029] Trioctyl trimellitate was manufactured using the following method. First, 100 grams of trimellitic anhydride (TMA) was melted in a melting vessel at 165°C to 170°C to provide molten TMA. Next, a four neck round bottom flask was equipped with a magnetic stirrer, an oil bath, a Dean-Stark apparatus, and a thermometer. Then 3.75 molar equivalents of 2-ethylhexyl alcohol, based on the amount of TMA, was added to the flask. The melt mixture formed a clear homogenous solution. The melt mixture was stirred and heated over the oil bath

at a temperature of 160°C. The catalyst (titanium tetra-isopropoxide) was added in an amount of 0.11 mole %, based on the moles of trimellitic anhydride.

[0030] After catalyst addition, immediate formation of water was observed. The water formed during the reaction was collected in the Dean-Stark apparatus. The Dean-Stark apparatus was drained of water periodically and the 2-ethylhexyl alcohol collected in the apparatus was returned to the reaction mixture. After 6 hours, the acid value of the product mixture was below 0.2. The product mixture was cooled to a temperature less than 100°C and prepared for distillation under vacuum. After setting the vacuum pressure to 7 to 8 millibars the product mixture temperature was slowly raised to 130°C to 150°C to 200°C to 230°C to remove most of the 2-ethylhexyl alcohol.

[0031] The temperature of the product mixture was then reduced to approximately 90°C and 3 milliliters of a caustic solution (49 weight percent of NaOH in water) was added and stirred for 30 to 40 minutes. The product mixture was purged with carbon dioxide for 20 to 30 minutes and the product mixture was distilled again under reduced pressure using the same method described above to remove water and remaining 2-ethylhexyl alcohol.

[0032] The temperature of the product mixture was reduced to approximately 110°C and then filtered over 1 gram of CELITE™ diatomaceous earth to remove a white solid and obtain a viscous liquid. The liquid was then contacted with 1 gram of charcoal at about 60-100°C and filtered over 1 gram of CELITE™ diatomaceous earth. The resulting tri(2-ethylhexyl) trimellitate (TOTM) product was tested for purity by gas chromatography (GC), refractive index, color, acid value, and specific gravity. The TOTM had a purity of 99.4 wt.%, a total ester content of 99.5 wt.%, both based on the total weight of the product, an APHA color value of 15, an acid value 0.05, a refractive index of 1.486, and a specific gravity at 22°C of 0.982.

The various embodiments are illustrated by the following aspects.

[0033] Aspect 1: A method of making trialkyl tricarboxylates comprising melting a phenyl tricarboxylic acid or anhydride thereof to provide a molten phenyl tricarboxylic acid or anhydride thereof; combining the molten phenyl tricarboxylic acid or anhydride thereof and greater than 3.0 molar equivalents of a C₄₋₁₈ alkyl alcohol, for example, greater than 3.5 molar equivalents of a C₄₋₁₈ alkyl alcohol, based on the total moles of phenyl tricarboxylic acid or an anhydride thereof, to provide a melt mixture; adding 0.05 mol% to 0.20 mol% of a titanium tetraalkoxide catalyst, based on the total moles of phenyl tricarboxylic acid or anhydride thereof, to the melt mixture to form a reaction mixture; reacting the phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol in the reaction mixture to form a product mixture having an acid value equal to or less than 0.5, preferably equal to or less than 0.3, more

preferably equal to or less than 0.2, as determined according to ASTM D1045, and comprising the trialkyl tricarboxylate; and isolating the trialkyl tricarboxylate from the product mixture.

[0034] Aspect 2: A method for sequential manufacture of trialkyl tricarboxylate and dioctyl phthalate in a reactor comprising manufacturing the trialkyl tricarboxylate in the reactor, wherein manufacturing the trialkyl tricarboxylate comprises melting a phenyl tricarboxylic acid or anhydride thereof to provide a molten phenyl tricarboxylic acid or anhydride thereof, combining the molten phenyl tricarboxylic acid or anhydride thereof and a C₄₋₁₈ alkyl alcohol to provide a melt mixture, adding a titanium tetraalkoxide catalyst to the melt mixture to form a reaction mixture, and reacting the phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol in the reaction mixture to form a product mixture comprising the trialkyl tricarboxylate; and manufacturing the dioctyl phthalate in the reactor, wherein manufacturing the dioctyl phthalate comprises reacting a phthalic anhydride with a C₄₋₁₈ alkyl alcohol in the presence of a homogeneous catalyst in the reactor to form a phthalate product mixture; and removing the product mixture comprising the trialkyl tricarboxylate from the reactor prior to manufacturing the dioctyl phthalate in the reactor or removing the phthalate product mixture from the reactor prior to manufacturing the trialkyl tricarboxylate in the reactor.

[0035] Aspect 3: The method of Aspect 2, further comprising manufacturing dioctyl terephthalate using the reactor.

[0036] Aspect 4: The method of one or more of the preceding Aspects, wherein melting the phenyl tricarboxylic acid or anhydride thereof comprises a temperature in a range of greater than 165°C to 190°C, preferably 165°C to 180°C, more preferably 165°C to 170°C.

[0037] Aspect 5: The method of one or more of the preceding Aspects, further comprising heating the C₄₋₁₈ alkyl alcohol to a temperature in a range of 80°C to 140°C, preferably 90°C to 130°C, more preferably 100°C to 120°C, prior to combining the molten phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol.

[0038] Aspect 6: The method of one or more of the preceding Aspects, wherein reacting the phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol comprises a temperature in a range of 150°C to 230°C, preferably 170°C to 230°C or 200°C to 220°C, more preferably 210°C to 215°C.

[0039] Aspect 7: The method of one or more of the preceding Aspects, wherein the reacting is for a reaction time equal to or less than 7 hours, preferably equal to or less than 6.5 hours, more preferably equal or less than 6 hours.

[0040] Aspect 8: The method of one or more of the preceding Aspects, wherein a purity of the trialkyl tricarboxylate is equal to or greater than 98.0 wt.%, preferably equal to or greater

than 98.5 wt.%, more preferably equal to or greater than 99.0 wt.%, based on the total weight of the trialkyl tricarboxylate.

[0041] Aspect 9: The method of one or more of the preceding Aspects, further comprising neutralizing the reaction mixture with an aqueous caustic solution, and purging the neutralized reaction mixture with carbon dioxide.

[0042] Aspect 10: The method of Aspect 9, further comprising distilling any residual C₄₋₁₈ alkyl alcohol from the reaction mixture prior to neutralizing, prior to purging, subsequent to purging, or a combination hereof.

[0043] Aspect 11: The method of Aspect 10, further comprising filtering the distilled reaction mixture after purging through a filter medium, contacting the filtered reaction mixture with charcoal, and filtering the charcoal containing mixture to produce a product having an acid value less than 0.1 and an APHA color value less than 30, preferably less than 20, more preferably less than 15, as determined according to ASTM D1045.

[0044] Aspect 12: The method of Aspect 11, wherein the filter media comprises diatomaceous earth, Fuller's earth, perlite, or combination thereof.

[0045] Aspect 13: The method of one or more of the preceding Aspects, wherein the phenyl tricarboxylic acid or anhydride thereof comprises trimellitic anhydride.

[0046] Aspect 14: The method of one or more of the preceding Aspects, wherein the C₄₋₁₈ alkyl alcohol comprises 2-ethylhexyl alcohol.

[0047] Aspect 15: The method of one or more of the preceding Aspects, wherein the titanium tetraalkoxide catalyst comprises titanium tetra-isopropoxide catalyst.

[0048] Aspect 16: A method for the manufacture of trialkyl tricarboxylate comprising melting a trimellitic anhydride to provide a molten trimellitic anhydride; combining the molten trimellitic anhydride and greater than 3.0 molar equivalents of 2-ethylhexyl alcohol, for example, greater than 3.5 molar equivalents of 2-ethylhexyl alcohol, based on the total moles of trimellitic anhydride, to provide a melt mixture; adding 0.05 mol% to 0.20 mol% of titanium tetra-isopropoxide catalyst, based on the total moles of trimellitic anhydride, to the melt mixture to form a reaction mixture; reacting the trimellitic anhydride and the 2-ethylhexyl alcohol in the reaction mixture to form a product mixture having an acid value equal to or less than 0.5, preferably equal to or less than 0.3, more preferably equal to or less than 0.2, as determined according to ASTM D1045, and comprising the trialkyl tricarboxylate; and isolating the trialkyl tricarboxylate from the product mixture.

[0049] Aspect 17: A trialkyl tricarboxylate manufactured by the method of any one or more of the preceding Aspects.

[0050] Aspect 18: A polymer composition comprising the trialkyl tricarboxylate of Aspect 17.

[0051] The compositions, methods, and articles can alternatively comprise, consist of, or consist essentially of, any appropriate materials, steps, or components herein disclosed. The compositions, methods, and articles can additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any materials (or species), steps, or components, that are otherwise not necessary to the achievement of the function or objectives of the compositions, methods, and articles.

[0052] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other (e.g., ranges of 5 wt.% to 20 wt.%", is inclusive of the endpoints and all intermediate values of the ranges of "5 wt.% to 25 wt.%, " etc.). "Combinations" is inclusive of blends, mixtures, alloys, reaction products, and the like. The terms "first," "second," and the like, do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. The terms "a" and "an" and "the" 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" unless clearly stated otherwise. Reference throughout the specification to "some embodiments" 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. A "combination thereof" is open and includes any combination comprising at least one of the listed components or properties optionally together with a like or equivalent component or property not listed

[0053] Unless specified to the contrary herein, all test standards are the most recent standard in effect as of the filing date of this application, or, if priority is claimed, the filing date of the earliest priority application in which the test standard appears.

[0054] 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 application belongs. All references are incorporated herein by reference in their entirety.

[0055] The term "alkyl" means a branched or straight chain, unsaturated aliphatic hydrocarbon group, e.g., methyl, ethyl, n-propyl, i-propyl, n-butyl, s-butyl, t-butyl, n-pentyl, s-pentyl, and n- and s-hexyl. The number of carbon atoms indicated in a group is exclusive of any substituents. For example -CH₂CH₂CN is a C₂ alkyl group substituted with a nitrile.

[0056] 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 method for the manufacture of a trialkyl tricarboxylate, the method comprising:
 - melting a phenyl tricarboxylic acid or anhydride thereof to provide a molten phenyl tricarboxylic acid or anhydride thereof;
 - combining the molten phenyl tricarboxylic acid or anhydride thereof and greater than 3.0 molar equivalents of a C₄₋₁₈ alkyl alcohol, for example, greater than 3.5 molar equivalents of a C₄₋₁₈ alkyl alcohol, based on the total moles of phenyl tricarboxylic acid or an anhydride thereof, to provide a melt mixture;
 - adding 0.05 mol% to 0.20 mol% of a homogeneous catalyst, preferably a titanium tetraalkoxide catalyst, based on the total moles of phenyl tricarboxylic acid or anhydride thereof, to the melt mixture to form a reaction mixture;
 - reacting the phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol in the reaction mixture to form a product mixture having an acid value equal to or less than 0.5, preferably equal to or less than 0.3, more preferably equal to or less than 0.2, as determined according to ASTM D1045, and comprising the trialkyl tricarboxylate; and
 - isolating the trialkyl tricarboxylate from the product mixture.
2. The method of claim 1, further comprising sequentially manufacturing the trialkyl tricarboxylate and a dioctyl phthalate in a reactor, the method comprising:
 - manufacturing the trialkyl tricarboxylate in the reactor;
 - manufacturing the dioctyl phthalate in the reactor, wherein manufacturing the dioctyl phthalate comprises reacting a phthalic anhydride with a C₄₋₁₈ alkyl alcohol in the presence of a homogeneous catalyst to form a phthalate product mixture; and
 - removing the product mixture comprising the trialkyl tricarboxylate from the reactor prior to manufacturing the dioctyl phthalate in the reactor or removing the phthalate product mixture from the reactor prior to manufacturing the trialkyl tricarboxylate in the reactor.
3. The method of Claim 2, further comprising manufacturing dioctyl terephthalate in the reactor.

4. The method of any one or more of the preceding claims, wherein melting the phenyl tricarboxylic acid or anhydride thereof comprises a temperature in a range of greater than 165°C to 190°C, preferably 165°C to 180°C, more preferably 165°C to 170°C.

5. The method of any one or more of the preceding claims, further comprising heating the C₄₋₁₈ alkyl alcohol to a temperature in a range of 80°C to 140°C, preferably 90°C to 130°C, more preferably 100°C to 120°C, prior to combining the molten phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol.

6. The method of any one or more of the preceding claims, wherein reacting the phenyl tricarboxylic acid or anhydride thereof and the C₄₋₁₈ alkyl alcohol comprises a temperature in a range of 150°C to 230°C, preferably 170°C to 230°C or 200°C to 220°C, more preferably 210°C to 215°C.

7. The method of any one or more of the preceding claims, wherein the reacting is for a reaction time equal to or less than 7 hours, preferably equal to or less than 6.5 hours, more preferably equal to or less than 6 hours.

8. The method of any one or more of the preceding claims, wherein a purity of the trialkyl tricarboxylate is equal to or greater than 98.0 wt.%, preferably equal to or greater than 98.5 wt.%, more preferably equal to or greater than 99.0 wt.%, based on the total weight of the trialkyl tricarboxylate.

9. The method of any one or more of the preceding claims, further comprising neutralizing the reaction mixture with an aqueous basic solution, and purging the neutralized reaction mixture with carbon dioxide.

10. The method of claim 9, further comprising distilling any residual C₄₋₁₈ alkyl alcohol from the reaction mixture prior to neutralizing, prior to purging, subsequent to purging, or a combination thereof.

11. The method of claim 10, further comprising:
filtering the distilled reaction mixture after purging through a filter medium,
contacting the filtered reaction mixture with a decolorizing agent, preferably charcoal,
and
filtering the decolorized mixture to produce a product having an acid value less than 0.1
as determined according to ASTM D1045, or an APHA color value less than 30, preferably less
than 20, more preferably less than 15, as determined in accordance with ASTM, or both.
12. The method of claim 11, wherein the filter media comprises diatomaceous earth,
Fuller's earth, perlite, or combination thereof.
13. The method of any one or more of the preceding claims, wherein the phenyl
tricarboxylic acid or anhydride thereof comprises trimellitic anhydride.
14. The method of any one or more of the preceding claims, wherein the C₄₋₁₈ alkyl
alcohol comprises 2-ethylhexyl alcohol.
15. The method of any one or more of the preceding claims, wherein the titanium
tetraalkoxide catalyst comprises titanium tetra-isopropoxide catalyst.
16. The method of any one or more of the preceding claims, comprising:
melting trimellitic anhydride to provide a molten trimellitic anhydride;
combining the molten trimellitic anhydride and greater than 3.0 molar equivalents of
2-ethylhexyl alcohol, for example, greater than 3.5 molar equivalents of 2-ethylhexyl alcohol,
based on the total moles of trimellitic anhydride, to provide the melt mixture;
adding 0.05 mol% to 0.20 mol% of titanium tetra-isopropoxide catalyst, based on the
total moles of trimellitic anhydride, to the melt mixture to form the reaction mixture;
reacting the trimellitic anhydride and the 2-ethylhexyl alcohol in the reaction mixture to
form the product mixture; and
isolating tri(2-ethylhexyl) trimellitate from the product mixture, having an acid value
equal to or less than 0.5, preferably equal to or less than 0.3, more preferably equal to or less
than 0.2, as determined according to ASTM D1045.
17. A trialkyl tricarboxylate manufactured by the method of any one or more of the
preceding claims.

18. A polymer composition comprising the trialkyl tricarboxylate of Claim 17.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/054826

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C67/08 C07C69/76 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) EPO-Internal, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2017/203434 A1 (SABIC GLOBAL TECHNOLOGIES BV [NL]) 30 November 2017 (2017-11-30) abstract examples 1-3 Embodiments 1-20 claims 1-20 paragraph [0001]	1-18
X	JP 2012 092074 A (MITSUBISHI GAS CHEMICAL CO) 17 May 2012 (2012-05-17) abstract examples claims 1-7	2,3,17, 18
☐ 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	Date of mailing of the international search report	
19 September 2019	27/09/2019	
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 Delanghe, Patrick	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2019/054826

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017203434 A1	30-11-2017	CN 109153630 A	04-01-2019
		EP 3464230 A1	10-04-2019
		WO 2017203434 A1	30-11-2017

JP 2012092074 A	17-05-2012	NONE	
