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(54) Title: PRODUCTION OF METHYL 2-ETHYLHEXYL TEREPHTHALATE AND BIS(2-ETHYLHEXYL) TEREPHTHALATE BLENDS

(57) Abstract: The invention provides methods of manufacturing blends of bis(2-ethylhexyl) terephthalate and methyl 2-ethylhexyl terephthalate. Bis(2-ethylhexyl) terephthalate and methyl 2-ethylhexyl terephthalate blends are useful as plasticizers in materials such as polyvinyl chloride. Bis(2-ethylhexyl) terephthalate and methyl 2-ethylhexyl terephthalate blends are prepared by a process of transesterification of dimethyl terephthalate with 2-ethylhexanol at elevated temperature to control the ratio of bis(2-ethylhexyl) terephthalate and methyl 2-ethylhexyl terephthalate in a product mixture.

PRODUCTION OF METHYL 2-ETHYLHEXYL TEREPHTHALATE AND BIS(2-ETHYLHEXYL) TEREPHTHALATE BLENDS

FIELD OF THE INVENTION

[0001] This invention pertains to the preparation of bis(2-ethylhexyl) terephthalate (DOTP) and methyl 2-ethylhexyl terephthalate (MOTP) from dimethyl terephthalate (DMT). More specifically, this invention pertains to a process for the preparation of DOTP and MOTP by the *trans*-esterification of dimethyl terephthalate with 2-ethylhexanol (2-EHOH) at elevated temperature to control the ratio of MOTP to DOTP in a product mixture.

BACKGROUND OF THE INVENTION

[0002] Bis(2-ethylhexyl) terephthalate, also known as dioctyl terephthalate or DOTP, is used as a plasticizer in a variety of polymeric materials such as polyvinyl chloride. DOTP is an alternative plasticizer to diisononyl phthalate (DINP). However, DOTP's performance is not always sufficient in many flexible polymers such as polyvinyl chloride (PVC) to replace DINP. A desirable replacement plasticizer will exceed the performance of DOTP while having a better cost position. A novel alternative to DINP is a blend of bis(2-ethylhexyl) terephthalate (DOTP) and methyl 2-ethylhexyl terephthalate (MOTP). The MOTP and DOTP plasticizer blend possesses a better performance profile than DOTP alone and is a viable alternative to DINP.

[0003] DOTP can be prepared by the titanate-catalyzed transesterification of dimethyl terephthalate (DMT) with 2-EHOH. Direct esterifications of TPA with 2-EHOH under conditions similar to those used for the transesterification of DMT have produced slow reaction rates and sporadic problems with foaming. US-2002028963-A1 discloses an esterification process wherein water is removed by azeotropic distillation together with an alcohol. JP-60004151-A (JP-03004052-B) discloses the reaction of TPA and 2-EHOH under elevated pressures and temperatures. JP 2001031794-A discloses the preparation of

terephthalic acid esters by reacting at least one of C9-C18 monohydric alcohol and 2-ethylhexanol with terephthalic acid. Finally, US-5,532,495 discloses a multi-step esterification process that includes removing water and a portion of the alcohol reactant from the reaction mixture.

[0004] A need exists for an efficient method to make MOTP and DOTP plasticizer blends that can be used as plasticizers in materials such as polyvinyl chloride.

BRIEF SUMMARY OF THE INVENTION

[0005] We have developed a process for the preparation of bis(2-ethylhexyl) terephthalate (DOTP) and methyl 2-ethylhexyl terephthalate (MOTP) by the esterification of TPA with 2-EHOH and methanol at elevated temperature and optionally elevated pressure.

[0006] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. reacting dimethyl terephthalate and 2-ethylhexanol in the presence of a catalyst while distilling methanol from said reaction;

b. monitoring the reaction of step a) to detect a desired DOTP/MOTP product distribution; and

c. recovering a DOTP/MOTP blend from said reaction.

[0007] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. adding dimethyl terephthalate, 2-ethylhexanol, a catalyst and an inert gas to a reactor to form a reaction mixture;

b. heating said reaction mixture of step a) to a desired temperature while monitoring said mixture to detect a desired DOTP and MOTP product distribution; and

c. recovering a DOTP and MOTP blend from said reaction mixture.

[0008] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. adding dimethyl terephthalate, 2-ethylhexanol, titanium(IV) isopropoxide and nitrogen to a reactor to form a reaction mixture;

b. heating said reaction mixture of step a) to a desired temperature, refluxing the reaction mixture and distilling methanol from said reaction mixture;

c. monitoring the reaction mixture of step b) to detect a desired DOTP/MOTP product distribution;

d. cooling said reaction mixture of step c);

e. adding an aqueous hydroxide solution to said reaction mixture of step d), to form a first aqueous component and a first organic component, said first organic component containing DOTP, MOTP and 2-ethylhexanol;

f. separating said first aqueous component of step e) from said first organic component of step e);

g. adding water to said first organic component of step f) to form a second aqueous component and a second organic component containing DOTP, MOTP and 2-ethylhexanol;

h. separating said second aqueous component from said second organic component of step g);

i. removing 2-ethylhexanol from said second organic component from step h) to form a mixture containing DOTP and MOTP; and

j. filtering and drying said solution of step i) to recover a DOTP/MOTP blend.

[0009] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. reacting dimethyl terephthalate and 2-ethylhexanol in the presence of a catalyst while distilling methanol from said reaction;

b. monitoring the reaction of step a) to a detect a desired amount of methanol; and

c. recovering a DOTP/MOTP blend from said reaction.

[0010] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. adding dimethyl terephthalate, 2-ethylhexanol, a catalyst and nitrogen to a reactor to form a reaction mixture;

b. heating said reaction mixture of step a) while distilling methanol from said reaction mixture;

c. monitoring the reaction mixture of step b) to detect a desired amount of methanol; and

d. recovering a DOTP and MOTP blend from said reaction mixture.

[0011] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP)blend comprising:

a. adding dimethyl terephthalate, 2-ethylhexanol, a catalyst and nitrogen to a reactor to form a reaction mixture;

b. heating said reaction mixture of step a) to a desired temperature, and distilling methanol from said reaction mixture:

c. monitoring the reaction mixture of step b) to detect a desired amount of methanol;

d. cooling said reaction mixture of step c);

e. adding an aqueous hydroxide solution to said reaction mixture of step d), to form a first aqueous component and a first organic component, said first organic component containing DOTP, MOTP and 2-ethylhexanol;

f. separating said first aqueous component of step e) from said first organic component of step e);

g. adding water to said first organic component of step f) to form a second aqueous component and a second organic component containing DOTP, MOTP and 2-ethylhexanol;

h. separating said second aqueous component from said second organic component of step g);

i. removing 2-ethylhexanol from said second organic component from step h) to form a mixture containing DOTP and MOTP; and

j. filtering and drying said solution of step i) to recover a DOTP/MOTP blend.

[0012] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. reacting DOTP and methanol in the presence of a catalyst while distilling methanol from said reaction;

b. monitoring the reaction of step a) to a detect a desired DOTP/MOTP product distribution; and

c. recovering a DOTP/MOTP blend from said reaction.

[0013] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. adding DOTP, methanol, a catalyst and nitrogen to a reactor to form a reaction mixture having a liquid phase and a gaseous phase;

b. heating said reaction mixture of step a), and distilling a gaseous mixture of methanol and 2-ethylhexanol from said reaction mixture gaseous phase of step a), and adding liquid methanol to said reaction mixture liquids phase of step a);

c. monitoring the reaction mixture of step b) to a detect a desired DOTP and MOTP product distribution; and

d. recovering a DOTP and MOTP blend from said reaction mixture.

[0014] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. adding DOTP, methanol, a catalyst and nitrogen to a reactor to form a reaction mixture having a liquid phase and a gaseous phase;

b. heating said reaction mixture of step a), and distilling a gaseous mixture of gaseous methanol and 2-ethylhexanol from said reaction mixture gaseous phase of step a), and adding liquid methanol to said reaction mixture liquids phase of step a);

c. monitoring the reaction mixture of step b) to a detect a desired DOTP/MOTP product distribution;

d. cooling said reaction mixture of step c);

e. adding an aqueous hydroxide solution to said reaction mixture of step d), to form a first aqueous component and a first organic component, said first organic component containing DOTP, MOTP and 2-ethylhexanol;

f. separating said first aqueous component of step e), from said first organic component of step e);

g. adding water to said first organic component of step f) to form a second aqueous component and a second organic component containing DOTP, MOTP and 2-ethylhexanol;

h. separating said second aqueous component from said second organic component of step g);

i. removing 2-ethylhexanol from said second organic component from step h) to form a mixture containing DOTP and MOTP; and

j. filtering and drying said solution of step i) to recover a DOTP/MOTP blend.

[0015] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. reacting terephthalic acid and 2-ethylhexanol in the presence of a catalyst to form a first reaction product;

b. reacting methanol with the first reaction product of step a) while monitoring the reaction of methanol and the first reaction product to a detect a desired DOTP/MOTP product distribution; and

c. recovering a DOTP/MOTP blend from said reaction.

[0016] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. heating a first reaction mixture of terephthalic acid and 2-ethylhexanol in the presence of a catalyst to form a first reaction product;

b. adding methanol to the first reaction product of step a), to form a second reaction mixture;

c. heating and monitoring the reaction mixture of step b) to a detect a desired DOTP and MOTP product distribution; and

d. recovering a DOTP and MOTP blend from said reaction mixture.

[0017] In one embodiment the invention is a method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. heating a first reaction mixture of terephthalic acid and 2-ethylhexanol in the presence of a catalyst to form a first reaction product;

b. adding methanol to the first reaction product of step a), to form a second reaction mixture;

c. heating and monitoring the reaction mixture of step b) to a detect a desired DOTP and MOTP product distribution;

d. cooling said reaction mixture of step c);

e. adding an aqueous hydroxide solution to said reaction mixture of step d), to form a first aqueous component and a first organic component, said first organic component containing DOTP, MOTP and 2-ethylhexanol;

f. separating said first aqueous component of step e) from said first organic component of step e);

g. adding water to said first organic component of step f) to form a second aqueous component and a second organic component containing DOTP, MOTP and 2-ethylhexanol;

h. separating said second aqueous component from said second organic component of step g);

i. removing 2-ethylhexanol from said second organic component from step h) to form a mixture containing DOTP and MOTP; and

j. filtering and drying said solution of step i) to recover a DOTP/MOTP blend.

DETAILED DESCRIPTION

Definitions

[0018] In this specification and in the claims that follow, reference will be made to a number of terms, which shall be defined to have the following meanings.

[0019] Values may be expressed as "about" or "approximately" a given number. Similarly, ranges may be expressed herein as from "about" one particular value and/or to "about" or another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another aspect.

[0020] As used herein, the terms "a," "an," and "the" mean one or more.

[0021] As used herein, the term "and/or," when used in a list of two or more items, means that any one of the listed items can be employed by itself or any combination of two or more of the listed items can be employed. For example, if a composition is described as containing components A, B, and/or C, the composition can contain A alone; B alone; C alone; A and B in combination; A and C in combination, B and C in combination; or A, B, and C in combination.

[0022] As used herein, the terms "comprising," "comprises," and "comprise" are open-ended transition terms used to transition from a subject recited before the term to one or more elements recited after the term, where the element or elements listed after the transition term are not necessarily the only elements that make up the subject.

[0023] As used herein, the terms “having,” “has,” and “have” have the same open-ended meaning as “comprising,” “comprises,” and “comprise” provided above.

[0024] As used herein, the terms “including,” “includes,” and “include” have the same open-ended meaning as “comprising,” “comprises,” and “comprise” provided above.

[0025] “Chosen from” as used herein can be used with “or” or “and.” For example, Y is chosen from A, B, and C means Y can be individually A, B, or C. Alternatively, Y is chosen from A, B, or C means Y can be individually A, B, or C, or a combination of A and B, A and C, B and C, or A, B, and C.

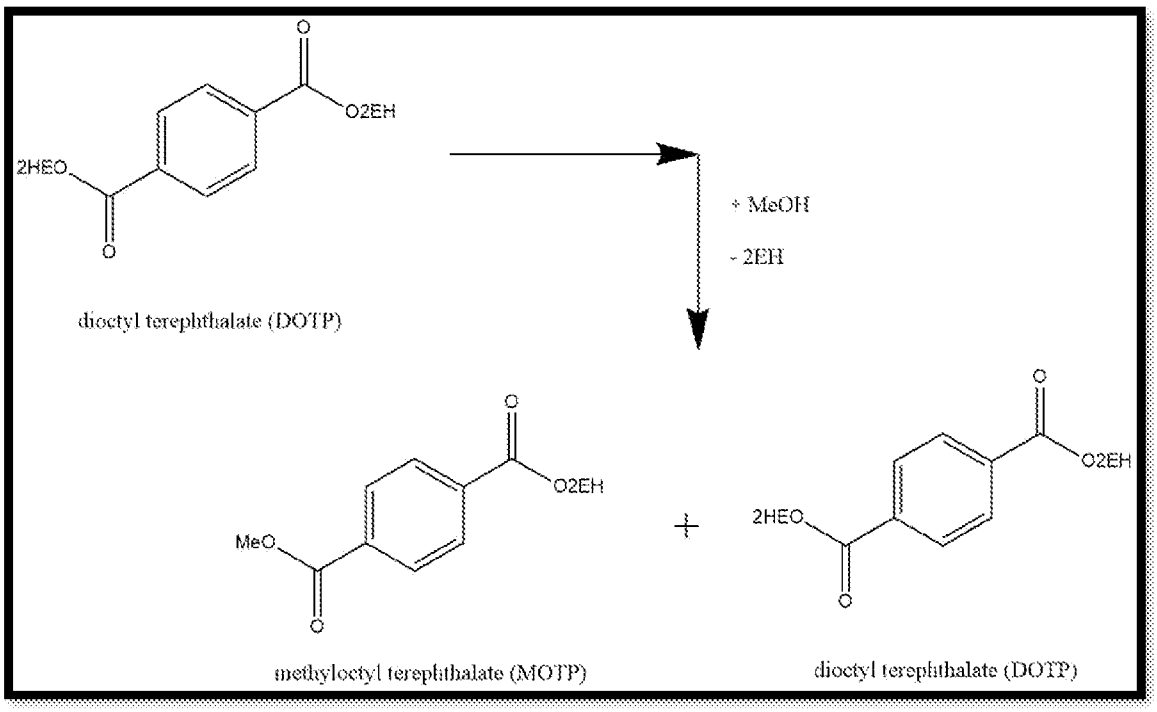
Invention

[0026] In an embodiment of this invention a batch or continuous reactor can be used in the conversion of dimethyl terephthalate to a bis(2-ethylhexyl) terephthalate and methyl 2-ethylhexyl terephthalate blend.

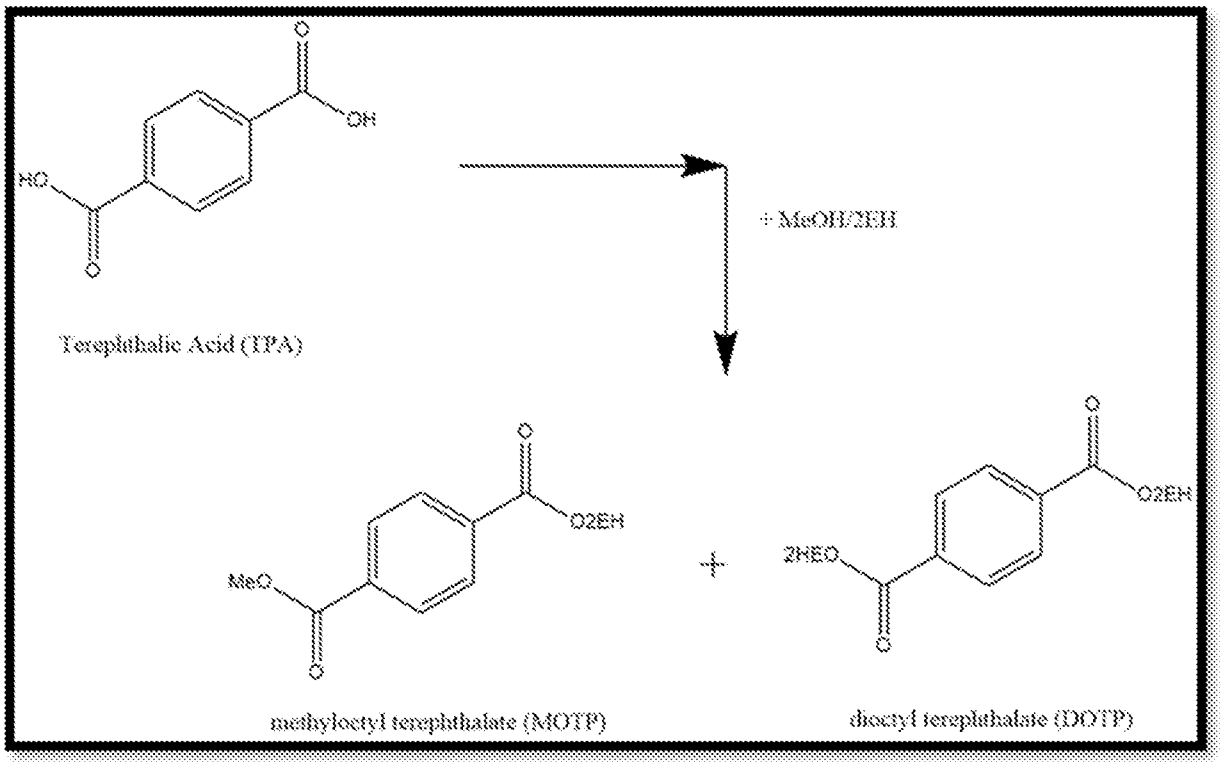
[0027] The simplest reactor for the method requires a vapor dividing head and access ports for charging material. The reactor is charged with dimethyl terephthalate, 2-ethylhexanol, and catalyst. The volatile by-product of the reaction is methanol and is removed by way of vapor dividing head to a pot temperature, then allowed to reflux. When the desired amount of methyloctyl terephthalate is reached, material is then treated with sodium hydroxide solution, decanted, then washed with water. This step will remove a majority of the remaining DMT. The excess 2-ethylhexanol is then stripped, and steam-stripped to remove residual amounts. After steam stripping the material is dried at reduced pressure, then filtered.

[0028] Another embodiment of this invention is a method of producing a MOTP and DOTP blend by monitoring the amount of methanol removed from the reaction mixture.

[0029] Another embodiment of this invention is a method of producing a MOTP and DOTP blend by transesterification of DOTP using methanol to achieve the MOTP and DOTP product blend desired.



[0030] Another embodiment of this invention is a method of producing a MOTP and DOTP blend by the mixed esterification reaction of terephthalic acid (TPA) and methanol/2-ethylhexanol. Because of the significant difference in the boiling points of methanol and 2-ethylhexanol, this reaction can be run under ambient or above ambient pressures.



[0031] In another embodiment of the invention the stoichiometric amount of 2-ethylhexanol can range from less than 2:1 (0 mol% excess) to 3:1 (50 mol% excess). The preferred amount is a 5 mol% excess of 2-ethylhexanol with the unreacted alcohol being recycled to the process. The amount of methyloctyl terephthalate produced is controlled by the pot temperature. At the preferred charge of 5 mol% excess of 2-ethylhexanol, a pot temperature of 160-176 °C produces 26.5-19.7% methyloctyl terephthalate. This range is consistent with the amount of methyloctyl terephthalate produced in the reaction mixture with excess 2-ethylhexanol remaining in the mixture. With the final material producing 23.04% at a pot temperature of 174 °C, 22.20% at a pot temperature of 176 °C, and 24.55% at a pot temperature of 170 °C. The target amount of methyloctyl terephthalate produced can be controlled by reactor temperature in batch or continuous process. The reactor temperature is also dependent upon the amount of 2-ethylhexanol that is charged to the reactor.

[0032] Suitable catalysts include strong protic acids such as tosylic, sulfuric, p-toluenesulfonic, phosphoric, and methanesulfonic acids, Lewis acids such as

compounds of tin, titanium, yttrium, zirconium, scandium and zinc, and alkali and alkaline earth metal salts and oxides such as BaO, SrO, CaO, MgO and LiCl. The preferred catalyst is tetraisopropyl titanate (TIPT).

EXAMPLES

[0033] This invention can be further illustrated by the following examples thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

[0034] Each example used the same equipment with the exception of reactor size. The material charges will be described for each example.

Abbreviations

[0035] mL is milliliter; wt % is weight percent; eq is equivalent(s); hrs or h is hour(s); mm is millimeter; m is meter; GC is gas chromatography; °C is degree Celsius; min is minute; tR is retention time; g is gram; mmol is millimole; mol is mole; kg is kilogram; L is liter; w/v is weight/volume; µL is microliter; Tg is glass transition temperature; MW is molecular weight.

Example 1

[0036] **Equipment:** Round bottom flask, stir bar, stir plate, 10" Penn State packed column, vapor dividing head, magnet for lifter, condenser, fraction cutter, receiver, and thermometers.

The molar ratio of each run is labeled.

240.9g 2-Ethylhexanol (mw-130.23; 1.85 moles)

194.2g DMT (mw-194.19; 1 mole)

0.23g TIPT (500ppm)

Table 1:

	Reaction	Base	Take-off	Take-off	
Time	Time (hrs)	Temp ºC	Temp ºC	vol (ml)	Comments
9:40	0	123	64	0	Start reaction time
10:55	1.25	225	65	57	Sample
11:40	2	224	65	60	Sample and shut down
2EHOH	DMT	Mono	DOTP		Sample ID
5.16%	1.07%	20.94%	72.38%		Sample at 225 °C initial temperature
4.33%	0.85%	19.01%	75.37%		Sample at 225 °C after 30-45 min hold, while still removing MeOH
4.71%	0.97%	18.94%	75.04%		Sample after cooling pot to 56 °C

Example 2

260.5g 2-Ethylhexanol (mw-130.23; 2 moles)

194.2g DMT (mw-194.19; 1 mole)

0.23g TIPT (500ppm)

Table 2:

	Reaction	Base	Take-off	Take-off	
Time	Time (hrs)	Temp ºC	Temp ºC	vol (ml)	Comments
10:50		125	64	0	start take-off at 25%
12:10		214	65	60	
12:20		222	65	61	Sample, changed pot temperature to 225 °C
1:00		225	65	63	Sample, changed pot temperature to 230 °C
1:40		230	65	64	Shut off sampled, then sampled in morning.
2EHOH	DMT	Mono	DOTP		Sample ID

6.67%	0.58%	15.64%	76.67%		220 °C sample
6.09%	0.46%	14.18%	78.84%		225 °C sample
6.42%	0.46%	14.06%	78.61%		230 °C sample

Example 3

Table 3 shows the same molar ratios as in example 2, but gradually increasing temperatures.

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Table 3:

	Reaction	Base	Take-off	Take-off	
Time	Time (hrs)	Temp ºC	Temp ºC	vol (ml)	Comments
11:25		118	65	0	start take-off
12:05		151	65	30	sample
12:30		190	65	54	stop take-off let reflux 30 min then sample
1:00		190	65	55	Sampled, raised set point to 200 °C
1:10		203	65	58	stop take-off let reflux 30 min then sample
1:40		201	65	58.5	Sampled, raised set point to 210 °C
1:50		212	65	60	stop take-off let reflux 30 min then sample
2:20		208	65	61	Sampled and shut down
2EHOH	DMT	Mono	DOTP		Sample ID
24.02%	6.36%	34.26%	35.02%		150 °C sample
8.96%	1.00%	19.68%	70.02%		190 °C sample
7.85%	0.75%	17.42%	73.62%		200 °C sample
6.78%	0.59%	15.88%	76.34%		210 °C sample

Example 4

[0037] Equipment: 1-L round bottom flask, stir bar, 10" Penn State packed column, vapor dividing head, condenser, fraction cutter, receiver, and thermocouples

[0038] Charges:

273.5g 2-Ethylhexanol (mw-130.23; 2.1 moles)

194.2g DMT (mw-194.19; 1 mole)

0.09g TIPT (200ppm)

[0039] Heat reaction stopping at 170C and gc for % mono in an effort to produce 20% monomethyl material.

[0040] After reaction was complete, the material was hazy at room temperature. Charged to a 1-L drop bottom flask, heat to 90 °C (at 30 °C pot was clear) and washed once with 2.5 wt% NaOH (200g) and once with DI Water (200g). The organic layer was then stripped to 150 °C at 7 mmHg, then steam stripped at 150 °C at 50 mmHg. After steam stripping, the material was dried. 321.3g material was produced.

Table 4:

	Reaction	Base	Take-off	Take-off	
Time	Time (hrs)	Temp ºC	Temp ºC	vol (ml)	Comments
9:10	0	159	63	0	Start reaction time and take-off
9:40	0.5	170	65	39	Stop take-off at pot temperature of 170 ºC Sample 1
10:40	1.5	170	65	45	Sample 2
11:20		176	65	46	Sample 3
12:00	2.9	176	65	46	Sample 4
2EHOH	DMT	Mono	DOTP		Sample ID
15.55%	2.30%	26.47%	55.42%		Sample 1
12.52%	1.24%	21.08%	64.88%		Sample 2
11.51%	1.08%	20.32%	66.81%		Sample 3
12.58%	1.11%	19.97%	66.01%		Sample 4

11.75%	1.05%	19.72%	67.19%		Final after work-up
11.84%	0.00%	19.99%	67.87%		After caustic and water wash
92.44%	0.00%	4.97%	1.48%		organic layer in take-off after steam strip
0.06%	0.00%	22.20%	77.41%		Final

Example 5

820.5g 2-Ethylhexanol (mw-130.23; 6.3 moles)

582.6g DMT (mw-194.19; 3 mole)

0.27g TIPT (200ppm)

[0041] Heat reaction stopping at 170 °C and gc for % monomethyl in an effort to produce 20% mono material.

[0042] After reaction was complete, the material was hazy at room temperature. Charged to a 5-L drop bottom flask, heated to 90 °C (at 30 °C pot was clear) and washed once with 2.5% NaOH (400g) and once with DI Water (400g), pH still acidic (5). Washed with 2.5 wt% NaOH (400g) and once with DI Water (400g) (pH 8). Decants went well, lot of solids in first caustic wash. The organic layer was then stripped to 150 °C at 7 mmHg, then nitrogen sparged at 150 °C at 50 mmHg. 1019.3g of material was produced.

Table 5:

	Reaction	Base	Take-off	Take-off	
Time	Time (hrs)	Temp ºC	Temp ºC	vol (ml)	Comments
12:15	0	146	63	0	Start reaction time and take-off
12:50		<120	60	25	Breaker flipped, heat shut off
1:10		118	64	25	start take-off
2:00		160	65	123	set point at 160 ºC in pot sample 1
2:30	2.25	157	65	140	shut off
8:30	2.25	145	65	140	Start take-off
8:40		155	65	150	
8:45	2.5	160	65	153	sample 2
9:20		162	65	154	Increase setpoint to 170 ºC
9:30	3.25	172	65	164	sample 3

10:30	4.25	174	65	165	shut off sample 4
2EHOH	DMT	Mono	DOTP		Sample ID
17.96%	2.30%	25.94%	53.53%		Sample 1
14.89%	1.88%	24.93%	58.03%		Sample 2
13.34%	1.41%	22.37%	65.29%		Sample 3
13.00%	1.17%	20.48%	65.04%		Sample 4
12.87%	0.33%	20.69%	65.80%		After caustic wash
12.99%	32.00%	20.62%	65.76%		After first water wash
12.67%	0.08%	20.83%	66.11%		After 2nd caustic wash
0.72%	0.08%	23.90%	74.96%		Before nitrogen sparge
0.05%	0.07%	23.17%	76.30%		Final
0.00%	0.05%	23.04%	75.68%		

Example 6

[0043] Example 6 is repeat of example 5.

820.5g 2-Ethylhexanol (mw-130.23; 6.3 moles)

582.6g DMT (mw-194.19; 3 mole)

0.27g TIPT (200ppm)

[0044] Heat reaction stopping at 170 °C and gc for % monomethyl in an effort to produce 20% mono material.

[0045] After reaction was complete, the material was hazy at room temperature. Charged to a 5-L drop bottom flask, heated to 70 °C (at 30 °C pot was clear) and washed twice with 2.5 wt% NaOH (400g) and once with DI Water (400g), pH 9. The organic layer was then stripped to 150 °C at 7 mmHg, then nitrogen sparged at 150 °C at 50 mmHg. 1001.1g of material was produced.

Table 6:

	Reaction	Base	Take-off	Take-off	
Time	Time (hrs)	Temp ºC	Temp ºC	vol (ml)	Comments
9:50	0	141	63	0	start take-off
10:50	1	168	65	155	lifter shuts off at pot temp of 170 ºC
10:52		170	65	160	

11:20	1.5	170	65	166	Sample 1
11:50	2	170	65	167	shut off, sample after cooling, sample 2
2EHOH	DMT	Mono	DOTP		Sample ID
16.01%	1.21%	20.22%	61.63%		Sample 1
13.36%	1.26%	21.14%	63.91%		Sample 2
13.60%	0.04%	21.52%	64.41%		Sample after 2nd caustic wash
0.06%	0.03%	24.55%	75.02%		Final

Example 7

[0046] Charges:

286.5g 2-Ethylhexanol (mw-130.23; 2.2 moles)

194.2g DMT (mw-194.19; 1 mole)

0.10g TIPT (200ppm)

Table 7:

	Reaction	Base	Take-off	Take-off	
Time	Time (hrs)	Temp ºC	Temp ºC	vol (ml)	Comments
10:45	0	143	63	0	Start take-off
11:05	0.3	154	64	25	lifter shut off at 155 ºC pot temperature
11:25	0.7	155	65	35	Sample 1, changed lifter shut off to a pot temp of 160 ºC
11:30	0.75	161	65	44	
12:00	1.25	163	65	46	Sample 2 at 160 ºC for thirty minutes
1:00	2.25	161	65	47	Sample 3
2:15	3.5	162	65	47	Shut down, sample 4 after cooled
9:35	3.5	22	22	47	Charged 26.0g 2-Ethylhexanol (0.2 moles), heat to reflux
10:00	3.5	132	63	47	Let reflux
10:30	4	151	64	47	Sample 5
11:30	5	151	64	47	Sample 6
12:30	6	152	64	47	Sample 7

2:00	7.5	154	64	48	Sample 8 and shut down
					Sample 9 after cooled to pot temp of 50 °C
2EHOH	DMT	Mono	DOTP		Sample ID
20.38%	2.33%	25.61%	51.40%		Sample 1
15.77%	1.32%	21.06%	61.56%		Sample 2
15.13%	1.22%	20.62%	62.72%		Sample 3
15.25%	1.18%	20.37%	62.87%		Sample 4
18.34%	1.07%	19.32%	60.91%		Sample 5
18.37%	0.99%	18.50%	61.83%		Sample 6
18.39%	0.96%	18.21%	62.13%		Sample 7
17.69%	0.89%	17.75%	63.37%		Sample 8
17.53%	0.89%	17.89%	63.39%		Sample 9

Example 8

390.7g 2-Ethylhexanol (mw-130.23; 3 moles)

194.2g DMT (mw-194.19; 1 mole)

0.29g TIPT (500ppm)

Table 8:

	Reaction	Base	Take-off	Take-off	
Time	Time (hrs)	Temp ºC	Temp ºC	vol (ml)	Comments
9:20		149	64	-	start take-off
9:50		156	65	46	
10:00		180	65	56	sample #1, pot temp at 183 °C set point at 180 °C
11:00		182	65	60	Sample #2 raise temperature
11:10		185	65	61	
12:10		190	65	62	sample #3 hold at 190 °C
1:10		192	65	62	Sample #4 shut down, reaction went too far

2EHOH	DMT	Mono	DOTP		Sample ID
23.74%	0.15%	7.51%	67.87%		sample #1
27.94%	0.08%	5.40%	66.26%		sample #2
22.67%	0.05%	4.21%	72.77%		sample #3
23.38%	0.12%	6.80%	69.40%		Sample #5 after cool-down

Example 9

[0047] **Equipment:** 1-L round bottom flask, stir bar, feed pump, feed tank, condenser, receiver, simple distillation head, and thermocouples

[0048] **Charges:**

585.9g DOTP(mw-390.6; 1.5 moles)

60g MeOH

0.6g TIPT (1000ppm)

[0049] A pot was set up for sub-surface MeOH addition and a simple distillation head. MeOH was charged to the pot prior to heating. GC samples were taken as temperature was increased.

Table 9:

	Base	Take-off	Take-off	Feed	
Time	Temp ºC	Temp ºC	vol (ml)	ml	Comments
9:45	77	64			
10:45	78	64			Sample 1
11:30	78	64			Sample 2
11:50	85	64			Remove MeOH
12:30	103	64			Removed ~35ml MeOH total
1:15	103	64			Sample 3; removed 66ml MeOH total-temp began slowly climbing in the pot
2:00	125	64			Sample 4
3:00	176	70			Shut down, sample 5
7:25	184	65	68	176	
7:45	206	65	68	176	drain ~2ml MeOH
8:15	211	63	70	176	start feed
8:17	204	64	70	170	

8:50	156	64	70	170	
9:25	176	65	72	170	
9:50	179	65	72	170	Sample 6
10:50	215	65	74	170	Add 4ml of MeOH
10:55	215	65	74	166	Remove pot MeOH to increase pot temp
12:20	225	41	81	165	start fee with Take-Off open
12:45	222	67	94	150	Sample 7 Heat to 240 °C
1:05	240	64	96	150	start feed
2:20	234	71	120	122	Heat to 250 °C sample 8
2:45	249	83	146	94	Shut off sample 9
8:55	250	29	0	196	
9:55	250	73	38	148	
10:35	250	73	68		Sample 11, shut off - when stopping take-off and continuing feed, vapor temperature rose to 188 °C
2EHOH	DMT	Mono	DOTP		Sample ID
0.00%	0.00%	2.37%	97.05%		Sample 1
0.00%	0.00%	2.43%	97.00%		Sample 2
0.00%	0.00%	2.44%	97.12%		Sample 3
0.00%	0.00%	2.48%	97.08%		Sample 4
0.00%	0.00%	2.63%	96.94%		Sample 5
0.00%	0.02%	3.19%	96.35%		Sample 6
0.00%	0.03%	3.66%	95.90%		Sample 7
0.00%	0.04%	4.23%	95.32%		Sample 8
1.81%	0.10%	6.49%	91.20%		Sample 9
5.73%	0.60%	16.27%	77.03%		Sample 10
7.37%	0.87%	18.81%	72.62%		Sample 11
7.81%	1.00%	20.17%	70.68%		Final

Example 10

[0050] Equipment: 1-L round bottom flask, stir bar, 10" Penn State packed column, decanter, feed pump, feed tank, condenser, receiver, and thermocouples.

[0051] Charges:

221.4g 2-ethylhexanol (mw 130.23; 1.7 moles)

166.1g TPA (mw 166.13; 1 mole)

0.387g TIPT (1000ppm)

28.4g 2-ethlyhexanol charged to decanter

[0052] A pot was set up for subsurface MeOH addition. The pot was heated to react 2-ethylhexanol with TPA and begin the MeOH subsurface feed after reaction was complete.

Table 10:

	Reaction	Base	Take-off	Take-off	Feed	
Time	Time (hrs)	Temp ºC	Temp ºC	vol (ml)	ml	Comments
12:30	0	234	97	-		water coming into decanter
1:30	1	242	173	7.7		
2:45	2.25	258	82	-		
3:00	2.5	267	81	7.1		Shut off; Sample 1
7:40	2.5	266	26	-	400	Begin MeOH feed
8:20		234	67	-		Let reflux- stop feed
8:55	3.25	267	63	-		start feed
9:05		266	65	18	370	
9:30		266	63	-		
10:20		256	69	55	330	Sample 2
10:55		265	68	90		
11:15		263	41	100		
11:45		281	64	-	300	Set point reached in base; Sample 3
12:15		280	115	160	260	
12:40		278	133	200	230	
1:00		279	110	225	200	Changed pot temperature to 285° C
1:35		285	106	300	145	Sample 4
2:30		287	95	300	25	Shut off; Sample 5
9:45		285	25	0	250	Changed feed to a 50:50 mole ratio of 2-ethylhexanol: MeOH
10:25		290	64	12	170	stopped feed let reflux 5 min.
12:50		286	105	68	0	stopped feed pot almost clear
12:55		288	130	70	130	
1:05		278	160	112	105	Pot appears clear, slight haze

1:55		287	126	230	25	Fed remaining feed fastest rate on pump
2:10		284	132	48	0	Shut off; sample 6
12:05		264	28	0	330	404.3g material in pot was clear, charged 21.6g of TPA to the pot to heat and begin MeOH only feed to see effects on the mono.
12:10		257	108	5	320	
12:55		265	112	84	260	
2:00		265	106	200	170	
2:15		265	106	224	140	
2EHOH	DMT	Mono	DOTP			Sample ID
22.18%	0.00%	0.00%	77.22%			Sample 1
34.99%	0.00%	0.87%	63.70%			Sample 2
16.55%	0.00%	0.43%	82.40%			Sample 3
13.13%	0.14%	7.13%	79.08%			Sample 4
4.20%	0.42%	13.39%	81.48%			Sample 5
9.65%	0.15%	8.24%	81.75%			Sample 6
4.26%	0.56%	15.72%	79.13%			Sample 7

[0053] In the specification, there have been disclosed certain embodiments of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being set forth in the following claims.

CLAIMS

We Claim:

1. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. reacting dimethyl terephthalate and 2-ethylhexanol in the presence of a catalyst while distilling methanol from said reaction;

b. monitoring the reaction of step a) to a detect a desired DOTP/MOTP product distribution; and

c. recovering a DOTP/MOTP blend from said reaction.

2. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. adding dimethyl terephthalate, 2-ethylhexanol, a catalyst and an inert gas to a reactor to form a reaction mixture;

b. heating said reaction mixture of step a) to a desired temperature while monitoring said mixture to detect a desired DOTP and MOTP product distribution; and

c. recovering a DOTP and MOTP blend from said reaction mixture.

3. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP)blend comprising:

a. adding dimethyl terephthalate, 2-ethylhexanol, titanium(IV) isopropoxide and nitrogen to a reactor to form a reaction mixture;

b. heating said reaction mixture of step a) to a desired temperature, distilling methanol from said reaction mixture and refluxing the reaction mixture;

c. monitoring the reaction mixture of step b) to detect a desired DOTP/MOTP product distribution;

d. cooling said reaction mixture of step c);

e. adding an aqueous hydroxide solution to said reaction mixture of step d), to form a first aqueous component and a first organic component, said first organic component containing DOTP, MOTP and 2-ethylhexanol;

f. separating said first aqueous component of step e) from said first organic component of step e);

g. adding water to said first organic component of step f) to form a second aqueous component and a second organic component containing DOTP, MOTP and 2-ethylhexanol;

h. separating said second aqueous component from said second organic component of step g);

i. removing 2-ethylhexanol from said second organic component from step h) to form a mixture containing DOTP and MOTP; and

j. filtering and drying said solution of step i) to recover a DOTP/MOTP blend.

4. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. reacting dimethyl terephthalate and 2-ethylhexanol in the presence of a catalyst while distilling methanol from said reaction;

b. monitoring the reaction of step a) to a detect a desired amount of methanol; and

c. recovering a DOTP/MOTP blend from said reaction.

5. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP)blend comprising:

a. adding dimethyl terephthalate, 2-ethylhexanol, a catalyst and nitrogen to a reactor to form a reaction mixture;

b. heating said reaction mixture of step a) while distilling methanol from said reaction mixture;

c. monitoring the reaction mixture of step b) to detect a desired amount of methanol; and

d. recovering a DOTP and MOTP blend from said reaction mixture.

6. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP)blend comprising:

a. adding dimethyl terephthalate, 2-ethylhexanol, a catalyst and nitrogen to a reactor to form a reaction mixture;

b. heating said reaction mixture of step a) to a desired temperature, and distilling methanol from said reaction mixture:

c. monitoring the reaction mixture of step b) to detect a desired amount of methanol;

d. cooling said reaction mixture of step c);

e. adding an aqueous hydroxide solution to said reaction mixture of step d), to form a first aqueous component and a first organic component, said first organic component containing DOTP, MOTP and 2-ethylhexanol;

f. separating said first aqueous component of step e) from said first organic component of step e);

g. adding water to said first organic component of step f) to form a second aqueous component and a second organic component containing DOTP, MOTP and 2-ethylhexanol;

h. separating said second aqueous component from said second organic component of step g);

i. removing 2-ethylhexanol from said second organic component from step h) to form a mixture containing DOTP and MOTP; and

j. filtering and drying said solution of step i) to recover a DOTP/MOTP blend.

7. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. reacting DOTP and methanol in the presence of a catalyst while distilling methanol from said reaction;

b. monitoring the reaction of step a) to a detect a desired DOTP/MOTP product distribution; and

c. recovering a DOTP/MOTP blend from said reaction.

8. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. adding DOTP, methanol, a catalyst and nitrogen to a reactor to form a reaction mixture having a liquid phase and a gaseous phase;

b. heating said reaction mixture of step a), and distilling a gaseous mixture of methanol and 2-ethylhexanol from said reaction mixture gaseous phase of step a), and adding liquid methanol to said reaction mixture liquids phase of step a);

c. monitoring the reaction mixture of step b) to a detect a desired DOTP and MOTP product distribution; and

d. recovering a DOTP and MOTP blend from said reaction mixture.

9. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP)blend comprising:

a. adding DOTP, methanol, a catalyst and nitrogen to a reactor to form a reaction mixture having a liquid phase and a gaseous phase;

b. heating said reaction mixture of step a), and distilling a gaseous mixture of gaseous methanol and 2-ethylhexanol from said reaction mixture gaseous phase of step a), and adding liquid methanol to said reaction mixture liquids phase of step a);

c. monitoring the reaction mixture of step b) to a detect a desired DOTP/MOTP product distribution;

d. cooling said reaction mixture of step c);

e. adding an aqueous hydroxide solution to said reaction mixture of step d), to form a first aqueous component and a first organic component, said first organic component containing DOTP, MOTP and 2-ethylhexanol;

f. separating said first aqueous component of step e), from said first organic component of step e);

g. adding water to said first organic component of step f) to form a second aqueous component and a second organic component containing DOTP, MOTP and 2-ethylhexanol;

h. separating said second aqueous component from said second organic component of step g);

i. removing 2-ethylhexanol from said second organic component from step h) to form a mixture containing DOTP and MOTP; and

j. filtering and drying said solution of step i) to recover a DOTP/MOTP blend.

10. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. reacting terephthalic acid and 2-ethylhexanol in the presence of a catalyst to form a first reaction product;

b. reacting methanol with the first reaction product of step a) while monitoring the reaction of methanol and the first reaction product to a detect a desired DOTP/MOTP product distribution; and

c. recovering a DOTP/MOTP blend from said reaction.

11. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP) blend comprising:

a. heating a first reaction mixture of terephthalic acid and 2-ethylhexanol in the presence of a catalyst to form a first reaction product;

b. adding methanol to the first reaction product of step a), to form a second reaction mixture;

c. heating and monitoring the reaction mixture of step b) to a detect a desired DOTP and MOTP product distribution; and

d. recovering a DOTP and MOTP blend from said reaction mixture.

12. A method of making a methyl 2-ethylhexyl terephthalate (MOTP) and bis(2-ethylhexyl) terephthalate (DOTP)blend comprising:

a. heating a first reaction mixture of terephthalic acid and 2-ethylhexanol in the presence of a catalyst to form a first reaction product;

b. adding methanol to the first reaction product of step a), to form a second reaction mixture;

c. heating and monitoring the reaction mixture of step b) to a detect a desired DOTP and MOTP product distribution;

d. cooling said reaction mixture of step c);

e. adding an aqueous hydroxide solution to said reaction mixture of step d), to form a first aqueous component and a first organic component, said first organic component containing DOTP, MOTP and 2-ethylhexanol;

f. separating said first aqueous component of step e) from said first organic component of step e);

g. adding water to said first organic component of step f) to form a second aqueous component and a second organic component containing DOTP, MOTP and 2-ethylhexanol;

h. separating said second aqueous component from said second organic component of step g);

i. removing 2-ethylhexanol from said second organic component from step h) to form a mixture containing DOTP and MOTP; and

j. filtering and drying said solution of step i) to recover a DOTP/MOTP blend.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2021/041351

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C67/08 C07C67/03 C07C69/82 C08K5/12
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 C08K

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, 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	RU 2 633 963 C2 (PUBLICHNOE AKTSIONERNOE OBSHCHESTVO SIBUR KHOLDING [RU]) 20 October 2017 (2017-10-20) paragraph [0089] - paragraph [0097] paragraph [0156] - paragraph [0170] examples 2-3, 12-13, 19-21; tables 1-2 -----	1-12
X	WO 2011/161037 A1 (BASF SE [DE]; WALTHER BURKHARD [DE] ET AL.) 29 December 2011 (2011-12-29) page 1, line 8 - line 11 page 29; examples claims -----	1-6

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
15 October 2021	25/10/2021

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2021/041351

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