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(71) **Applicant: BLUE CUBE IP LLC** [US/US]; 190 Carondelet Plaza, Suite 1530, Clayton, Missouri 63105 (US).

(72) **Inventors: TIRTOWIDJOJO, Max**; c/o BLUE CUBE IP LLC, 190 Carondelet Plaza, Suite 1530, Clayton, Missouri 63105 (US). **LUEBBE, Thomas**; c/o BLUE CUBE IP LLC, 190 Carondelet Plaza, Suite 1530, Clayton, Missouri 63105 (US). **MYERS, John D.**; c/o BLUE CUBE IP LLC, 190 Carondelet Plaza, Suite 1530, Clayton, Missouri 63105 (US). **SELL, Marc**; c/o BLUE CUBE IP LLC, 190 Carondelet Plaza, Suite 1530, Clayton, Missouri 63105 (US).

(74) **Agent: CRAWFORD, Bradley** et al.; POLSINELLI PC, 105 West Vandalia Street, Suite 400, Edwardsville, Illinois 62025 (US).

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(54) Title: IMPROVED PROCESS FOR LIQUID PHASE CHLORINATION OF CHLORINATED ALKENES

(57) **Abstract:** The present invention provides processes for the production of chlorinated alkanes from at least one chlorinated alkenes using a chlorinating agent in a two reactor system.

IMPROVED PROCESS FOR LIQUID PHASE CHLORINATION OF CHLORINATED ALKENES

FIELD OF THE INVENTION

[0001] The present disclosure generally relates to the preparation of chlorinated alkanes from chlorinated alkenes.

BACKGROUND OF THE INVENTION

[0002] Chlorinated alkanes are useful as products and intermediates for a variety of agricultural products, pharmaceuticals, blowing agents, solvents, gums, and refrigerants. The chlorination of alkenes is widely known. Generally, a chlorinating agent is reacted with an alkene, either in liquid or gas phase wherein the chlorinating is used in excess. Even though these processes are very efficient and produce high yields of the chlorinated alkane, these processes have drawbacks with respect to increased by-product formation and the use of large quantities of the chlorinating agent, especially chlorine gas. The excess chlorinating agent is normally removed from the process and transferred to waste where the chlorinating agent is quenched and disposed. The processes have higher unit manufacturing cost and large waste factors due to quenching and disposal of the chlorinating agent.

[0003] One highly sought group of chlorinated alkanes are pentachloropropanes, especially 1,1,1,2,3-pentachloropropane (240db) and 1,1,1,2,3,3-hexachloropropane. These chlorinated propanes are useful in agricultural products and intermediates for the next generation refrigerants. Processes to produce chlorinated propanes can be either in gas phase or liquid phase using excess chlorine gas. These processes can be run to completion where the chlorinated propene starting materials are consumed in the process (high percent conversion) or they can be run at lower conversion to reduce by-product formation. Yet, since an excess of chlorine is normally used, the processes have higher manufacturing cost, have large chlorine capture and recycle strategies, and large waste factors for treating and disposing of the excess chlorine.

[0004] US 9,416,073 teaches a process for chlorinating a chloroolefin. The processes comprise chlorinating a chloroolefin using an excess of chlorinating agent, in a first reactor. The reaction mixture from the first reactor then enters a second reactor, which contains fresh chloroolefin and is equipped to receive fresh chloroolefin. The excess chlorinating agent then reacts with the fresh chloroolefin to thereby form a chloroalkane product. Unreacted chloroolefin from the second reactor is then recycled to the first reactor.

[0005] Developing a simplified process for the production of chlorinated alkanes would be advantageous. Such processes would reduce manufacturing costs, reduce the amount of waste produced, and utilize lower amounts of chlorine in the process.

SUMMARY OF THE INVENTION

[0006] In one aspect, disclosed herein are processes for preparing chlorinated alkane products. In general, the process comprises forming a liquid reaction mixture comprising at least one chlorinated alkene starting material, optionally a solvent, and a chlorinating agent, wherein there is a gas phase above the liquid reaction mixture. After generating the liquid reaction mixture, a first liquid reaction product is produced comprising the at least one chlorinated alkene starting material, the chlorinated alkane product, the chlorinating agent dissolved in the liquid reaction mixture, and optionally a solvent. At least a portion of the first liquid product, and optionally, additional chlorinated alkene, is transferred to a second reactor. Additional reactors, in parallel or series, may be used. In the second reactor, the residual chlorinating agent dissolved in the first liquid product continues to react with the at least one chlorinated alkene starting material until greater than 80% of the chlorinating agent is consumed, thereby forming a second liquid reaction product. At least a portion of the second liquid reaction product is distilled and at least a portion of the chlorinated alkane product is separated from the chlorinated alkene. A residual chlorinating alkene stream is generated. In all embodiments, additional chlorinating agent is not added to the second reactor.

[0007] In another aspect, disclosed herein are processes for preparing 1,1,1,2,3-pentachloropropane from 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof. In general, the process comprises forming a liquid reaction mixture comprising 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, optionally a solvent, and a gas phase comprising a chlorinating agent. After generating the liquid reaction mixture, a first liquid reaction product is produced comprising 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof, 1,1,1,2,3-pentachloropropane, the chlorinating agent dissolved in the liquid reaction mixture, and optionally a solvent. At least a portion of the first liquid product is transferred to a second reactor. In the second reactor, the residual chlorinating agent dissolved in the first liquid product continues to react with the 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof until greater than 80% of the chlorinating agent is consumed forming a second liquid reaction product. At least a second portion of the second liquid reaction product is distilled and at least a portion of the 1,1,1,2,3-pentachloropropane is separated from the 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof. A residual stream comprising 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof is generated. In all embodiments, neither additional chlorinating agent nor additional chloroolefin is added to the second reactor.

[0008] In yet another aspect, disclosed herein are processes for preparing 1,1,1,2,3,3-hexachloropropane from 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof. In general, the process comprises forming a liquid reaction mixture comprising 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, optionally a solvent, and a gas phase comprising a chlorinating agent. After generating the liquid reaction mixture, a first liquid reaction product is produced comprising 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof, 1,1,1,2,3,3-hexachloropropane, the chlorinating agent dissolved in the liquid reaction mixture, and optionally a solvent. At least a portion of the first liquid product is transferred to a second reactor. In the second reactor, the residual chlorinating agent dissolved in the first liquid product continues to react with the 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof until greater than 80% of the chlorinating agent is consumed forming a second liquid reaction product. At least a second portion of the second liquid reaction product is distilled and at least a portion of the 1,1,1,2,3,3-hexachloropropane is separated from the 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof. A stream comprising residual 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof is generated. In all embodiments, neither additional chlorinating agent nor additional chloroolefin is added to the second reactor.

[0009] In still another aspect, disclosed herein are processes for preparing 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof, from 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof. In general, the process comprises forming a liquid reaction mixture comprising 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof, optionally a solvent, and a gas phase comprising a chlorinating agent. After generating the liquid reaction mixture, a first liquid reaction product is produced comprising 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof, 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof, the chlorinating agent dissolved in the liquid reaction mixture, and optionally a solvent. At least a portion of the first liquid product is transferred to a second reactor. In the second reactor, the residual chlorinating agent dissolved in the first liquid product continues to react with the 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof until greater than 80% of the chlorinating agent is consumed forming a second liquid reaction product. At least a second portion of the second liquid reaction product is distilled and at least a portion of the 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof is separated from the 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof. A residual stream comprising 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof is generated. In all embodiments, neither additional chlorinating agent nor additional chloroolefin is added to the second reactor.

[0010] Other features and iterations of the invention are described in more detail below.

DETAILED DESCRIPTION OF THE INVENTION

[0011] In one aspect, the process for preparing the chlorinated alkane product comprises generating a liquid reaction mixture by contacting at least one chlorinated alkene starting material, optionally a solvent, and a gas phase comprising a chlorinating agent. After generating the liquid reaction mixture, a first liquid reaction product is produced comprising the at least one chlorinated alkene starting material, the chlorinated alkane product, the chlorinating agent dissolved in the liquid reaction mixture, and optionally a solvent. At least a portion of the first liquid product is transferred to a second reactor. In the second reactor, the residual chlorinating agent dissolved in the first liquid product continues to react until greater than 80% of the chlorinating agent is consumed forming a second liquid reaction product. At least a portion of the second liquid reaction product is distilled and at least a portion of the chlorinated alkane product is separated from the chlorinated alkene starting material. A residual chlorinated alkene stream is generated. Preferably, at least some, if not all of the residual chlorinated alkene and/or any residual chlorinating agent is/are recycled to the first reactor. In all embodiments, neither additional chlorinating agent nor additional chloroolefin is added to the second reactor.

(I) Process to Prepare First Liquid Reaction Product

[0012] The process to form the first liquid reaction product commences by contacting at least one chlorinated alkene starting material, a gas phase comprising a chlorinating agent, and an optional solvent, in a reactor.

(a) chlorinated alkene starting material

[0013] A wide variety of chlorinated alkenes may be used in the liquid reaction mixture. Generally, the at least one chlorinated alkene may comprise between 2 to 6 carbon atoms and may be linear, branched or cyclic. In some embodiments, the chlorinated alkene is a chlorinated propene. Non-limiting examples of chlorinated propenes include monochlorinated propenes, dichlorinated propenes, trichlorinated propenes, tetrachlorinated propenes, pentachlorinated propenes, or combinations thereof. Non-limiting examples of linear chlorinated alkenes include vinyl chloride, allyl chloride (3-chloropropene), 2-chloropropene, 1-chloropropene isomers, 1,3-dichloropropene, 2,3-dichloropropene, 3,3-dichloropropene, 1,2,3-trichloropropene, 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,1,2,3-tetrachloropropene, 2-chloro-1-butene, 3-chloro-1-butene, 2-chloro-2-butene, 1,4-dichloro-2-butene, 3,4-dichloro-1-butene, 1,3-dichloro-2-butene, 2,3,4-trichloro-1-butene, 1,2,3,4-tetrachloro-2-butene, 1,1,2,4-tetrachloro-1-butene, 2,3-dichloro-1,3-butadiene, 1-chloro-3-methyl-2-butene, 3-chloro-3-methyl-butene, 5-chloro-1-pentene, 4-chloro-1-pentene, 3-chloro-1-pentene, 3-chloro-2-pentene, 1,2-dichloro-1-pentene, 1,1,5-trichloro-1-pentene, 6-chloro-1-hexene, 1,2-dichloro-1-hexene, and combinations thereof. Non-limiting examples of cyclic chlorinated alkenes include 1-chlorocyclopentene, 2-chlorocyclopentene, 3-chlorocyclopentene, 1,2-dichlorocyclopentene, 4,4-dichlorocyclopentene, 3,4-dichlorocyclopentene, 1-chloro-1,3-cyclopentadiene, 2-chloro-1,3-cyclopentadiene, 5-chloro-1,3-cyclopentadiene, 1,2-dichloro-1,3-cyclopentadiene, 1,3-dichloro-1,3-cyclopentadiene, 1,4-dichloro-1,3-cyclopentadiene, 5,5-dichloro-1,3-cyclopentadiene, 1,2,3-trichloro-1,3-cyclopentadiene, 1,2,3,4-tetrachloro-1,3-cyclopentadiene, 1-chloro-1,3-cyclohexadiene, and 3-chloro-1,4-cyclohexyldiene. As will be apparent to the person skilled in the art, the starting chlorinated alkene or chlorinated alkenes dictate which chlorinated alkane or alkanes will be formed.

[0014] In one embodiment, the chlorinated alkene comprises 1,1,3-trichloropropene, 3,3,3-trichloropropene, or combinations thereof. In another embodiment, the chlorinated alkene comprise 1,1,3,3-tetrachloropropene; 1,3,3,3-tetrachloropropene, or combinations thereof. In yet another embodiment, the chlorinated alkene starting material comprises 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof.

(b) optional solvent

[0015] In various embodiments, the reaction mixture may further comprise a solvent. Non-limiting examples of solvents may be CCl_4, C_2Cl_4 (tetrachloroethylene), the chloroalkene starting material, the chlorinated alkane product, or combinations thereof. In a preferred embodiment, the solvent comprises carbon tetrachloride.

(c) chlorinating agent

[0016] The chlorinating agent comprises chlorine. Chlorine may be used at a pressure that is at least atmospheric pressure or at sub-atmospheric pressures. The chlorine gas may be diluted with a carrier gas, such as nitrogen, a noble gas, or combinations thereof. Preferably, the pressure of the chlorine gas, and the entire reaction, is at least atmospheric pressure.

[0017] The chlorinating agent may be introduced into the headspace above the liquid phase reaction, and thus, at least some of the chlorinating agent is in the gas phase, or below the surface of the liquid phase (sub-surface introduction). In one embodiment, the chlorinating agent is diluted in an inert gas before it enters the first reactor. In another embodiment, at least some of the chlorinating agent is dissolved in the liquid reaction medium before the at least one chlorinated alkene starting material is added to the first reactor.

[0018] Generally, the mole ratio of the chlorinating agent to the chloroalkane starting material may range from about 0.01:1.0 to about 0.99:1.0. In various embodiments, the mole ratio of the chlorinating agent to the chloroalkane starting material may range from about 0.01:1.0 to about 0.99:1.0, from about 0.1:1.0 to about 0.95:1.0, from about 0.2:1.0 to about 0.9:1.0, from about 0.3:1.0 to about 0.8:1.0, from about 0.4:1.0 to about 0.7:1.0, from about 0.45:1.0 to about 0.55:1.0. As appreciated by the skilled artisan, the product distribution of the chlorinated alkene starting material and the chlorinated alkane product will be dependent on the mole ratio of the chlorinating agent to the chlorinated alkene starting material used in the process.

(d) reaction conditions

[0019] The processes disclosed herein may be run in a batch mode, semi-batch mode, or a continuous mode, with continuous mode preferred. Additionally the processes are conducted in a reactor that is resistant to, if not inert to the reaction conditions disclosed herein. Reactors may be made from materials such as Hastelloy, tantalum, or glass.

[0020] In a continuous mode, the first reactor may be a continuous stirred tank reactor, plug flow reactor, or a jet loop reactor. In a preferred embodiment, the first reactor is continuous stirred tank reactor. The reactor as described above may also comprise at least one eductor nozzle, at least one draft tube, at least one liquid jet, or combinations thereof. The addition of the at least one eductor nozzle, at least one draft tube, at least one liquid jet, or combinations thereof additionally aid in the interactions of the components in the first reactor improving the process kinetics and shortening the reaction time.

[0021] The reaction mixture may be stirred by using at least one eductor nozzle, at least one liquid jet, or combinations thereof which creates turbulence in the liquid phase. The at least one eductor nozzle, at least one liquid jet, or combinations thereof may be positioned below the surface of the liquid phase, thereby creating turbulence in the liquid phase and providing increased mixing. The at least one eductor nozzle, at least one liquid jet, or combinations thereof may be positioned at the surface of the reaction mixture or above the surface of the reaction mixture directed into the reaction mixture, thereby providing increased turbulence of the reaction mixture and mixing the gaseous and liquid components of the reaction mixture.

[0022] At least one draft tube may also be utilized. The draft tube provides an internal recirculation of the reaction mixture. The circulation may be induced by energy from the at least one liquid jet, from the at least one gas educting nozzle, from rising gas bubbles within the reactor, or a combination thereof.

[0023] Jet mixing may also utilize at least one eductor, at least one liquid jet, or combinations thereof. In this configuration, as described above, increased turbulence in the reaction mixture but also increased gas absorption of the gas into the liquid phase may be realized.

[0024] At least one of the above described mixing/stirring methods or a combination thereof, may be utilized in the processes disclosed herein. In one embodiment, a stream comprising one or more of the residual chlorinated alkene stream, the chlorinated alkene starting material, the first liquid reaction product, or combinations thereof, is used to educt the gas phase comprising the chlorinating agent into the liquid reaction mixture.

[0025] In general, the process for the preparation of chlorinated alkane product in the first reactor will be conducted to maintain the temperature from about 0°C to about 110°C utilizing either an internal or external heat device or a cooling device. In various embodiments, the temperature of the reaction may be maintained from about 0°C to about 110°C, from 10°C to about 70°C, or from about 15°C to about 50°C.

[0026] Generally, the process may be conducted at a pressure of 14 psi (atmospheric) to about 1000 psi so the reaction may proceed and maintain the kinetics of the process. In various embodiments, the pressure of the process may be from about 14 psi to about 1000 psi, from 14.7 to 500 psi, from about 14.7 psi to about 300 psi, or from 14.7 psi to about 200 psi.

[0027] In general, the reaction is allowed to proceed for a sufficient period of time until at least 50% of the chlorinated alkene starting material is converted into the chlorinated alkane product in the first product mixture as compared to the total contents of the first liquid reaction product as determined by any method known to one skilled in the art, such as chromatography (e.g., GC-gas chromatography). In various embodiments, the reaction is allowed to proceed for a sufficient period of time until at least 50%, at least 60%, at least 70%, at least 80%, at least 90%, at least 95% of the chlorinated alkene starting material is converted into the chlorinated alkane product in the first product mixture.

[0028] The duration of the reaction may range from about 5 minutes to about 12 hours. In some embodiments, the duration of the reaction may range from about 5 minutes to about 12 hours, from about 30 minutes to about 10 hours, from about 1 hour to about 6 hours, or from about 2 hours to about 4 hours.

[0029] In one embodiment, a feed comprising the at least one chlorinated alkene is continuously added to the first reactor.

(e) output from first reactor.

[0030] The output from the first reactor comprises the at least one chlorinated alkene starting material, unreacted chlorinating agent, an optional solvent, and the at least one chlorinated alkane product in the first liquid reaction product. Generally, the at least one chlorinated alkane product in the first liquid reaction product is greater than 50% by weight as compared to the total contents of the first liquid product mixture. In various embodiments, the chlorinated alkane product in the first liquid reaction product is greater than 50%, greater than 60%, greater than 70%, greater than 80%, or even greater than 90% as compared to the total contents of the first liquid reaction product.

(II) Process to Prepare Second Liquid Reaction Product

[0031] At least a portion of the first liquid reaction product comprising the at least one chlorinated alkene starting material, unreacted chlorinating agent, an optional solvent, and the at least one chlorinated alkane product is transferred to a second reactor. In the second reactor, the remaining chlorinating agent continues to react with the chlorinated alkene starting material and thereby form the chlorinated alkane product. The second reactor is commonly known as a “finishing reactor.”

(a) first liquid reaction product

[0032] The first liquid reaction product is described above in Section (I)(e). The chlorinating agent leaving the first reactor is dissolved in the first liquid reaction product. It is preferred that liquid chlorinating agents are the only chlorinating agents present in the second reactor.

(b) reaction conditions

[0033] The reaction conditions suitable for use in the second reactor are described above. The reaction conditions in the second reactor need not be the same as those in the first reactor, although they can be. If the first reactor is a continuous stirred tank reactor (CSTR), then the second reactor is not a plug flow reactor. If the first reactor is a plug flow reactor, the second reactor is not a CSTR. In one embodiment, both reactors are CSTRs. In another embodiment, both reactors are plug flow reactors.

[0034] In general, the process for the preparation of chlorinated alkane product in the first reactor will be conducted to maintain the temperature from about 0°C to about 110°C utilizing either an internal or external heat device or a cooling device. In various embodiments, the temperature of the process may be maintained from about 0°C to about 110°C, from 10°C to about 70°C, or from about 15°C to about 50°C.

[0035] Generally, the process may be conducted at a pressure of 14 psi (atmospheric) to about 1000 psi so the reaction may proceed and maintain the kinetics of the process. In various embodiments, the pressure of the process may be from about 14 psi to about 1000 psi, from 14.7 to 500 psi, from about 14.7 psi to about 300 psi, or from 14.7 psig to about 200 psi. The pressure in the second reactor may be lower than the first reactor since no additional chlorinating agent is added.

[0036] In general, the reaction is allowed to proceed for a sufficient period of time until at least 80% of the chlorinated alkene starting material is converted into the chlorinated alkane product in the second liquid reaction product as compared to the total contents of the second liquid reaction product as determined by any method known to one skilled in the art, such as chromatography (e.g., GC-gas chromatography). In various embodiments, the reaction is allowed to proceed for a sufficient period of time until at least 80%, at least 85%, at least 90%, at least 95%, at least 99% of the chlorinated alkene starting material is converted into the chlorinated alkane product in the second liquid reaction product.

[0037] In one embodiment, in the second reactor, at least 80% of the dissolved chlorinating agent is consumed. Preferably, at least 85% of the chlorinating agent is consumed. In another embodiment, at least 90 % of the chlorinating agent is consumed. In still another embodiment, at least 95% or at least 97% or at least 99% of the chlorinating agent is consumed.

[0038] The duration of the reaction may range from about 5 minutes to about 12 hours. In some embodiments, the duration of the reaction may range from about 5 minutes to about 12 hours, from about 30 minutes to about 10 hours, from about 1 hour to about 6 hours, or from about 2 hours to about 4 hours.

(c) output from second reactor

[0039] The output from the second reactor comprises the at least one chlorinated alkene starting material, residual chlorinating agent, an optional solvent, and the at least one chlorinated alkane product in the second liquid reaction product. Generally, the at least one chlorinated alkane product in the second liquid reaction product is greater than 80% as compared to the total content of the second liquid product mixture as determined by any method known to one skilled in the art, such as chromatography (e.g., GC-gas chromatography). In various embodiments, the at least one chlorinated alkane product in the second liquid reaction product is greater than 80%, greater than 85%, greater than 90%, greater than 95%, or even greater than 99% as compared to the total contents of the second liquid reaction product.

(III) Separation of the Chlorinated Alkane Product and Recycle Streams

[0040] The separation of the chlorinated alkane product from the second liquid product mixture comprises transferring a least a portion of the second liquid product mixture to a separator. Removal of the unreacted chlorinated alkene starting material and residual chlorinating agent(s) produces a chlorinated alkane product with high purity. If desired, additional purification steps may be used to increase the purity of the chlorinated alkane product.

[0041] In various embodiments, the separator may be a distillation column or a multistage distillation column which comprises at least one theoretical plate. Non-limiting examples of distillations may be a simple distillation or a vacuum distillation. Additionally, the separator may further comprise a reboiler, a bottom stage, or a combination thereof. Various distillation columns may be used in this capacity. In one embodiment, a side draw column or a distillation column which provides outlet stream from an intermediate stage or a dividing wall column (dividing wall column (DWC) is a single shell, fully thermally coupled distillation column capable of separating mixtures of three or more components into high purity products (product effluent streams)) may be used as a separator where the product effluent streams comprise chlorinated alkene starting material, the chlorinated alkane product, residual chlorinating agent, light by-products, heavy by-products, or combinations thereof. At least a portion of the various product effluent streams produced by the process may be recycled back to the first reactor or captured to provide increased kinetics, increased efficiencies, reduced overall cost of the process, increased selectivity and yield of the desired chlorinated alkane product. In one embodiment, the second liquid reaction product is distilled and the chlorinated alkane product is separated from the chlorinated alkene, which thereby generates a residual chlorinated alkene stream, wherein at least a portion of the chlorinated alkene stream is recycled to the first reactor and/or to other additional reactors – if used. If desired, the residual chlorinated alkene stream may be further distilled to remove impurities or to isolate particular reactants, and each stream may independently be recycled to the first reactor.

[0042] Each effluent stream, as described below, is enriched in the particular component of the liquid phase reaction mixture. Further separations may be required to produce highly pure compounds. If more than one reactant is to be recycled to the first reactor, then there is no need to separate each reactant. Instead, a mixture of two or of the two or more reactants can be recycled to the first reactor. For example, in one purification protocol, the second liquid reaction product enters a distillation column and the residual Cl_2, alkene and solvent (if present) is removed as an overhead stream and recycled to the first reactor. This mixture may be further purified before it is recycled to the first reactor.

[0043] In another embodiment, the process may be conducted in a reactive distillation column. In this configuration, the chemical reactor and a distillation step are combined in a single operating step, thus, allowing for simultaneous addition of reactants into the process, formation of various product streams, and distillation of the various product streams.

[0044] A portion of the second reaction liquid product is then transferred into a separator. In an embodiment, the separator may utilize at least one simple distillation, at least one vacuum distillation, at least one fractional distillation, or combinations thereof. The distillations may comprise at least one theoretical plate.

[0045] As appreciated by the skilled artisan, separating the purified chlorinated alkane product from the second liquid product mixture would produce at least two product effluent streams. In various embodiments, separating the purified chlorinated alkane product may produce three product effluent streams, four product effluent streams, or more product streams depending on the separation device utilized.

[0046] In an embodiment, the liquid reaction mixture is distilled, and the lights, comprising the chlorinating agent (typically chlorine) are removed. The chlorinating agent may be purified and then recycled to the first reactor. In the same distillation column or in a different distillation column, the chlorinated alkene can also be separated from the liquid reaction mixture. The chlorinated alkene can be recycled to the first reactor and chlorinated, to thereby generate the chlorinated alkane product. Alternatively, the chlorinated alkene can be chlorinated in a separate reactor, or isolated as a pure product. Again, in the same distillation column or in a different distillation column, the chlorinated alkane product can be isolated. Heavies can be removed from the bottom of one or more distillation columns. The heavies are optionally recycled to the reactor.

[0047] In an alternate embodiment, the lights (comprising chlorinating agent) are removed as one stream, while the chlorinated alkene and the chlorinated alkane product are removed as a second stream. The lights containing stream can be further distilled to purify the chlorinating agent (typically chlorine), which may be recycled to the first reactor. The heavies can be recycled to the reactor or discarded.

[0048] As an example, the separation of the chlorinated alkane product from the contents of the second liquid product mixture using three product streams is described below.

[0049] The second reaction liquid product may be distilled to produce three product streams, product effluent streams (a), (b), and (c). Product effluent stream (a) comprises the optional solvent, light by-products, residual chlorinating agent, and optionally at least a portion of the residual chlorinated alkene starting material which under the process conditions described above is removed as a gas as an overhead stream during the separation. Optionally, product effluent stream (b) comprises the chlorinated alkene starting material, optionally at least a portion of the residual chlorinating agent, and optionally at least a portion of the optional solvent, which may be removed as a side stream. In other embodiments, product effluent stream (b) is not formed. In such a case, (a) is further distilled to remove light byproducts and (c) may be further purified to remove the heavies. Product (c) comprises chlorinated alkane product and heavy by-products. Product (c) is the bottom stream.

[0050] Product effluent stream (c) may be further purified producing two additional product effluent streams (f) and (g) wherein product effluent stream (f) comprises the at least one chlorinated alkane product and product effluent stream (g) comprises heavy by-products.

[0051] In order to improve the efficiency of the process, various product effluent streams may be externally recycled back into the process. In various embodiments, at least a portion of the product effluent stream (b) comprising chlorinated alkene starting material, product effluent stream (d), and/or product effluent stream (e) comprising the optional solvent are recycled to the first reactor.

[0052] In another embodiment, at least a portion of b) comprising chlorinated alkene starting material, product effluent stream (d), and product effluent stream (e) comprising the optional solvent may be mixed with fresh liquid feed (comprising the chlorinating agent, non-recycled chlorinated alkene starting material and optional solvent) before being recycled back into the reactor in batch mode or continuous mode. In various embodiments, the product effluent streams and fresh liquid and gas feeds may be introduced into the reactor separately or mixed together before entering the process. To be clear, fresh feed streams may contain all or less than all of the following: the chlorinating agent, the chlorinated alkene starting material, and the optional solvent. The introduction of these fresh liquid feeds into the reactor or mixing the recycle streams with fresh liquid feeds increases the efficiency of the process, reduces the overall cost, maintains the kinetics, maintains the reaction conversion, increase the through-put, and reduces the by-products produced by the process. The amounts of the product effluent streams recycled to the reactor or fresh liquid feeds added to the reactor may be the same or different. One way to measure the amount of product effluent streams and/or fresh liquid feeds being added to the reactor is to identify the mass flow of the materials. The product effluent stream being recycled to the reactor has a product effluent stream mass flow, while the fresh liquid feeds being added to the reactor has a fresh liquid feed mass flow. Mass flows may be measured using methods known in the art.

[0053] Generally, the mass of the product effluent stream mass flow being recycled to the fresh liquid feed mass flow is adjusted to not only maintain the conversion of the process but also maintain the kinetics of the process.

[0054] Product effluent stream (f) from the separator comprising the at least one chlorinated alkane product produced in the chlorination process may have a yield of at least about 10%. In various embodiments, product effluent stream (f) comprising chlorinated alkane produced in the process may have a yield of at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

[0055] Product effluent stream (f) comprising the at least one chlorinated alkane product may have a weight% of the chlorinated alkane product of at least 95 wt%. In various embodiments, the weight percentage of the chlorinated alkane product may be at least 95 wt%, at least 96 wt%, at least 97 wt%, at least 98 wt%, at least 99 wt%, or at least 99.5 wt%.

(IV). Preferred Embodiments: Preparation of 1,1,1,2,3-Pentaachloropropane from 1,1,3-Trichloropropene; 3,3,3-Trichloropropene, or Combinations Thereof

(a) process to prepare first liquid reaction product comprising 1,1,1,2,3-pentachloropropane

[0056] In an aspect, disclosed herein are processes for preparing 1,1,1,2,3-pentachloropropane. The first portion of the process is described in Section (I). The process commences by combining 1,1,3-trichloropropene; 3,3,3-trichloropropene, or combinations thereof, a gas phase comprising a chlorinating agent, and an optional solvent in the first reactor generating the first liquid reaction product.

(b) process to prepare second liquid reaction product comprising 1,1,1,2,3-pentachloropropane

[0057] The overall process for forming the second liquid product mixture comprising 1,1,1,2,3-pentachloropropane is described above in Section (II). The reaction conditions used in preparing the second liquid product mixture are described above in Section (II)(b).

[0058] The output from the second reactor comprises the 1,1,3-trichloropropene; 3,3,3-trichloropropene, or combinations thereof, residual chlorinating agent, an optional solvent, and 1,1,1,2,3-pentachloropropane in the second liquid reaction product.

(c) *separation of the 1,1,1,2,3-pentachloropropane and recycle streams*

[0059] The process for separating the 1,1,1,2,3-pentachloropropane from the second liquid product mixture is described above in Section (III).

(V). Preferred Embodiments: Preparation of 1,1,1,2,3,3-Hexachloropropane from 1,1,3,3-Tetrachloropropene; 1,3,3,3-Tetrachloropropene, or Combinations Thereof

(a) process to prepare first liquid reaction product comprising 1,1,1,2,3,3-hexachloropropane

[0060] Another aspect of the present disclosure encompasses process for preparing 1,1,1,2,3,3-hexachloropropane. The first portion of the process is described in Section (I). The process commences by combining 1,1,3,3-tetrachloropropene; 1,3,3,3-tetrachloropropene, or combinations thereof, a gas phase comprising a chlorinating agent, and an optional solvent in the first reactor generating the first liquid reaction product.

(b) process to prepare second liquid product mixture comprising 1,1,1,2,3,3-hexachloropropane

[0061] The process to form the second liquid product mixture comprising 1,1,1,2,3,3-hexachloropropane is described above in Section (II).

[0062] The output from the second reactor comprises the 1,1,3,3-tetrachloropropene; 1,3,3,3-tetrachloropropene, or combinations thereof, residual chlorinating agent, an optional solvent, and 1,1,1,2,3,3-hexachloropropane in the second liquid product mixture.

(c) *separation of the 1,1,1,2,3,3-hexachloropropane and recycle streams*

[0063] The process for separating the 1,1,1,2,3,3-hexachloropropane from the second liquid product mixture is described above in Section (III).

(VI). Preferred Embodiments: Preparation of 1,2,2,3-Tetrachloropropane, 1,1,1,2,3-Pentachloropropane, 1,1,2,2,3-Pentachloropropane, or Combinations Thereof, from 1,1,3-Trichloropropene; 3,3,3-Trichloropropene, 1,2,3-Trichloropropene, 2,3-Dichloropropene, or Combinations Thereof

(a) process to prepare first liquid reaction product comprising 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof

[0064] Another aspect of the present disclosure encompasses process for preparing 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof. The process commences by combining 1,1,3-trichloropropene; 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof, a gas phase comprising a chlorinating agent, and an optional solvent in the first reactor generating the first liquid reaction product. The gas phase comprising the chlorinating agent is described above in Section (I)(c).

The optional solvent is described above in Section (I)(b). The reaction conditions are described above in Section (I)(d).

[0065] In general, the reaction is allowed to proceed for a sufficient period of time until at least 50% of the 1,1,3-trichloropropene; 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof is converted into the 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof in the first liquid reaction product as compared to the total contents of the first liquid reaction product as determined by any method known to one skilled in the art, such as chromatography (e.g., GC-gas chromatography). In various embodiments, the reaction is allowed to proceed for a sufficient period of time until at least 50%, at least 60%, at least 70%, at least 80%, at least 90% of 1,1,3-trichloropropene; 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof is converted into 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof in the first liquid reaction product.

[0066] The output from the first reactor comprises 1,1,3-trichloropropene; 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof, unreacted chlorinating agent, an optional solvent, and the 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof in the first liquid reaction product. Generally, the 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof in the first liquid reaction product is greater than 50% as compared to the total contents of the first liquid reaction product. In various embodiments, the 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof in the first liquid reaction product is greater than 50%, greater than 60%, greater than 70%, greater than 80%, or even greater than 90% as compared to the total contents of the first liquid reaction product.

(b) process to prepare second liquid product mixture comprising 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof

[0067] The process to form the second liquid product mixture comprising 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof is described above in Section (II). The reaction conditions used in preparing the second liquid product mixture is described above in Section (II)(b).

[0068] The output from the second reactor comprises the 1,1,3-trichloropropene; 3,3,3-trichloropropene; 1,2,3-trichloropropene; 2,3-dichloropropene; or combinations thereof, residual chlorinating agent, an optional solvent, and 1,2,2,3-tetrachloropropane; 1,1,1,2,3-pentachloropropane; 1,1,2,2,3-pentachloropropane; or combinations thereof in the second liquid product mixture. Generally, the 1,2,2,3-tetrachloropropane; 1,1,1,2,3-pentachloropropane; 1,1,2,2,3-pentachloropropane; or combinations thereof in the second liquid product mixture is greater than 80% as compared to the total contents of the second liquid product mixture as determined by any method known to one skilled in the art, such as chromatography (e.g., GC-gas chromatography). In various embodiments, the 1,2,2,3-tetrachloropropane; 1,1,1,2,3-pentachloropropane; 1,1,2,2,3-pentachloropropane; or combinations thereof in the second liquid product mixture is greater than 80%, greater than 85%, greater than 90%, greater than 95%, or even greater than 99% as compared to the total contents of the second liquid product mixture.

(c) *separation of the 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof and recycle streams*

[0069] The process for separating the 1,2,2,3-tetrachloropropane; 1,1,1,2,3-pentachloropropane; 1,1,2,2,3-pentachloropropane; or combinations thereof from the second liquid product mixture is described above in Section (III). Specific recycle streams useful in improving the efficiency of the process are described above in Section (III).

[0070] Product effluent stream (f) from the separator comprising the 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof produced in the chlorination process may have a yield of at least about 10%. In various embodiments, product effluent stream (f) comprising the 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof in the process may have a yield of at least about 20%, at least about 50%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 95%, or at least about 99%.

[0071] Product effluent stream (f) comprising the 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof may have a weight% of at least 95 wt%. In various embodiments, the weight percentage of the 1,1,1,2,3-pentachloropropane may have a weight percentage of at least 95 wt%, of at least 96 wt%, of at least 97 wt%, of at least 98 wt%, of at least 99 wt%, or at least 99.5 wt%.

DEFINITIONS

[0072] When introducing elements of the embodiments described herein, the articles "a", "an", "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising", "including" and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

[0073] Having described the invention in detail, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.

CLAIMS

What is claimed is:

1. A method of preparing chlorinated alkanes, the method comprises:

combining at least one chlorinated alkene starting material, a chlorinating agent, and optionally a solvent, in a first reactor and thereby forming a liquid reaction mixture having a gas phase above the liquid reaction mixture;

generating a first liquid reaction product comprising chlorinated alkene starting material, chlorinated alkane product, chlorinating agent dissolved in the liquid reaction mixture, and optionally a solvent;

transferring at least a portion of the first liquid reaction product, and optionally, additional chlorinated alkene, to a second reactor and/or other additional reactors, where residual chlorinating agent dissolved in the liquid reaction mixture continues to react with the chlorinated alkene until greater than 80% of the chlorinating agent is consumed, and a second liquid reaction product is formed;

wherein additional chlorinating agent is not added to the second reactor.

2. The method of claim 1, wherein at least a portion of the second liquid reaction product is distilled and the chlorinated alkane product is separated from the chlorinated alkene and thereby generating a residual chlorinated alkene stream.

3. The method of claim 2, wherein the residual chlorinated alkene stream is recycled to the first reactor and/or to the other additional reactors.

4. The method of any of the claims 1-3, wherein the pressure in the first reactor is maintained at least in part, by adding gas phase comprising a chlorinating agent.

5. The method of any one of claims 1-4, wherein the first reactor is a continuous stirred tank reactor, a plug flow reactor, or a jet loop reactor.

6. The method of claim 5, wherein the first reactor comprises at least one eductor nozzle, at least one draft tube, or combinations thereof.

7. The method of any one of claims 5 or 6, wherein the first reactor is a continuous stirred tank reactor and the second reactor is a plug flow reactor.

8. The methods of any one of the claims 1-7, wherein a feed comprising the at least one chlorinated alkene is continuously added to the first reactor.

9. The method of any one of the claims 6-8, wherein a stream comprising one or more of the residual chlorinated alkene stream, the chlorinated alkene starting material, the first liquid reaction product, or combinations thereof, is used to educt the gas phase comprising the chlorinating agent into the liquid reaction mixture.

10. The method of any one of the claims 1-9, wherein the liquid phase further comprises a solvent comprising CCl_4.

11. The method of any one of the claims 1-10, wherein the chlorinating agent comprises chlorine.

12. The method of any one of the claims 1-11, wherein the chlorinated alkene is a chlorinated propene.

13. The method of claim 12, wherein the chlorinated propene comprises 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,3,3,3-tetrachloropropene, 1,1,3,3-tetrachloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, a monochloropropene isomer, or combinations thereof.

14. The method of any one of the claims 1-13, wherein the chlorinated alkane is a chlorinated propane.

15. The method of claim 14, wherein the chlorinated propane comprises at least two chlorine atoms.

16. The method of either claims 14 or 15, wherein the chlorinated propane comprises 1,2,2,3-tetrachloropropane; 1,1,1,2,3-pentachloropropane; 1,1,2,2,3-pentachloropropane; 1,1,1,2,2,3-hexachloropropane or combinations thereof.

17. The methods of claims 1-16, wherein the pressure of the continuous reactor is from about 14.7 psi (atmospheric) to about 1000 psi or preferably from 14.7 psi to 200 psig.

18. The methods of any one of the claims 1-17, wherein the liquid phase reaction temperature is from about 0°C to about 110°C and preferably from about 10°C to about 70°C and more preferably from about 15°C to about 50°C.

19. The methods of any one of the claims 1-18, wherein the concentration of the chlorinated alkane in the first reaction product mixture is greater than 50% as compared to the total contents of the first product mixture.

20. The methods of any one of the claims 1-19, wherein at least 50% of the chlorinated alkene is converted into the chlorinated alkane in the first product mixture.

21. The methods of any one of the claims 1-20, wherein the concentration of the chlorinated alkane in the second product mixture is greater than 80% as compared to the total contents of the second product mixture.

22. The methods of any one of the claims 1-21, wherein at least 80% of the chlorinated alkene is converted into the chlorinated alkane in the second product mixture.

23. A method according to any one of claims 1-22, wherein the chlorinated alkane product comprises 1,1,1,2,3-pentachloropropane; the chlorinated alkene starting material comprises 1,1,3-trichloropropene; 3,3,3-trichloropropene or combinations thereof; and the chlorinating agent comprises chlorine.

24. A method according to any one of claims 1-22, wherein the chlorinated alkane product comprises 1,1,1,2,3,3-hexachloropropane; the chlorinated alkene starting material comprises 1,1,3,3-tetrachloropropene, 1,3,3,3-tetrachloropropene, or combinations thereof; and the chlorinating agent comprises chlorine.

25. A method according to any one of claims 1-22, wherein the chlorinated alkane product comprises 1,2,2,3-tetrachloropropane, 1,1,1,2,3-pentachloropropane, 1,1,2,2,3-pentachloropropane, or combinations thereof; the chlorinated alkene starting material comprises 1,1,3-trichloropropene, 3,3,3-trichloropropene, 1,2,3-trichloropropene, 2,3-dichloropropene, or combinations thereof; and the chlorinating agent comprises chlorine.

26. A method according to any one of claims 1-25, wherein at least a portion of the second liquid reaction product is distilled and the chlorinating agent is separated from the second liquid reaction product and recycled to the first reactor.

27. A method according to any one of claims 1-26, wherein_a catalyst comprising metallic iron, carbon steel, or iron alloy is contained within the first reactor, the second reactor, or both.

28. A method according to any one of claims 1-27, wherein at least some of the chlorinating agent is diluted in an inert gas before it enters the first reactor.

29. A method according to any one claims 1-27, wherein at least some of the chlorinating agent is dissolved in the liquid reaction medium before the at least one chlorinated alkene starting material is added to the first reactor.

30. A method according to any one of claims 1-29, wherein, in the second reactor, the chlorinating agent dissolved in the liquid reaction mixture continues to react with the chlorinated alkene until greater than 90% of the chlorinating agent is consumed.

31. A method according to any one of claims 1-30, wherein, in the second reactor, the chlorinating agent dissolved in the liquid reaction mixture continues to react with the chlorinated alkene until greater than 95% of the chlorinating agent is consumed.

32. A method according to any one of claims 1-31, wherein, in the second reactor, the chlorinating agent dissolved in the liquid reaction mixture continues to react with the chlorinated alkene until greater than 99% of the chlorinating agent is consumed.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/047850

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C17/04 C07C19/01
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 2016/058568 A1 (SPOLEK [CZ]) 21 April 2016 (2016-04-21) page 11 lines 13-19, page 18 lines 6-11, page 19 lines 1-2,; claim 1; examples 1, 3, 6 -----	1-32
X	JP 2012 056920 A (TOKUYAMA CORP) 22 March 2012 (2012-03-22) claim 1; figure 1 -----	1-32

☐ 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

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"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

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Date of the actual completion of the international search 22 November 2019	Date of mailing of the international search report 29/11/2019
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 Hacking, Michiel

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2019/047850

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