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HONEYWELL INTERNATIONAL INC.
101 COLUMBIA ROAD
P O BOX 2245
MORRISTOWN, NJ 07962-2245

FILING RECEIPT



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Date Mailed: 03/26/2008

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If Required, Foreign Filing License Granted: 03/25/2008

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 61/036,526**

Projected Publication Date: None, application is not eligible for pre-grant publication

Non-Publication Request: No

Early Publication Request: No

Title

Process of Co-Producing HFC-1225ye and HFC-1234yf via 4-step reactions

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Title 37, Code of Federal Regulations, 5.11 & 5.15

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PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS

5 CROSS-REFERENCES TO RELATED APPLICATIONS

This application is related to and claims the priority benefit of.....

.....

Also incorporated herein by reference are of the following U.S. Applications
10 which are filed concurrently herewith and identified by Attorney Docket Nos.
H0012514-4510; and H0013128-4511.

BACKGROUND OF THE INVENTION

Fluorinated olefins, as a class, have many and varied uses, including as
15 chemical intermediates and monomers, refrigerants, blowing agents, propellants and
solvents.

Several methods for preparing fluorinated olefins are known. For example,
U.S. Patent No. 5,679,875 discloses methods for manufacturing 1,1,1,2,3-
pentafluoropropene and 1,1,1,2,3-pentafluoropropane; U.S. Patent No. 6,031,141
20 discloses a catalytic process using chromium-containing catalysts for the
dehydrofluorination of hydrofluorocarbons to fluoroolefins; U.S. Patent No. 5,396,000
discloses a process for producing $\text{CF}_3\text{CHFCH}_2\text{F}$ using vapor phase catalytic
dehydrohalogenation to produce $\text{CF}_3\text{CF}=\text{CHF}$ and HF, followed by vapor phase
catalytic hydrogenation of $\text{CF}_3\text{CF}=\text{CHF}$ in the presence of HF; U.S. Patent No.
25 6,548,719 discloses a process for producing fluoroolefins by dehydrohalogenating a
hydrofluorocarbon in the presence of a phase transfer catalyst; U.S. Publication No.
2006/0106263 discloses the production and purification of hydrofluoroolefin
compounds; and WO98/33755 discloses catalytic process for the dehydrofluorination
of hexafluoropropanes to pentafluoropropenes.

Applicants have come to appreciate that substantial economic hurdles are present in connection with development of commercial process for the production of certain desirable fluorinated olefins. For example, the cost would be relatively high to build a commercial production facility that is capable of producing in efficient and effective fashion the fluoroolefin 1,1,1,2,3-pentafluoropropane (HFO-1225yf). However, applicants have come to appreciate that there are circumstances in which such a molecule is not as desirable for certain applications as other fluoroolefins. For example, applicants have come to appreciate that 1,1,1,2-tetrafluoropropane (HFO-1234yf) is more preferred than HFO-1225yf for certain refrigerant and blowing agent applications. As a result, it might become economically prohibitive to build a processing facility to produce each of these desirable fluorinated olefins.

Applicants have previously developed a process for producing HFO-1234yf which involves hydrogenating HFO-1225yf to produce 1,1,1,2,3-pentafluoropropane (HFC-245eb) and then using the HFC-245eb as a reactant in a dehydrofluorination reaction to produce HFO-1234yf. Applicants have also previously developed a process for producing HFO-1225yf which involves first hydrogenating hexafluoropropylene (HFP) to produce 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and then using the HFC-236ea as a reactant in a dehydrogenation reaction to produce HFO-1225yf. Therefore, according to these prior processes, a total of four separate unit operations would be required to be utilized in a commercial plant in order for the plant to have the flexibility to make both fluorinated olefins in a wide range of relative proportions.

In addition to the above-noted problem, applicants have come to appreciate that certain fluorinated olefins, particularly HFO-1225yf, can be a desirable starting material to the production of other more fluorinated olefins that might be more desirably for certain applications, including particularly HFO-1234yf.

In view of applicants' recognition of the above-noted problems and features of prior processes, applicants have developed improved processes that are capable of achieving substantial economic advantage in capital cost as well as substantial

flexibility and advantage in the actual operation to maximize efficiency and production of a range of fluorinated olefins.

SUMMARY OF THE INVENTION

5 The present invention provides in one aspect methods of producing fluorinated olefins, preferably fluorinated olefins having from 3 to 6 carbon atoms and at least 4 fluorine substituents, and even more preferably at least one fluorinated olefin selected from the group consisting of 1,1,1,2-tetrafluoropropene (HFO-1234yf), 1,1,1,2,3-pentafluoropropene (HFO1225ye) and combinations of these. The methods
10 preferably comprise: hydrogenating at least one highly fluorinated olefin, preferably a fluorinated propene having a degree of fluorination of N+1, and even more preferably at least five fluorine substituents (ie., N = 4 or greater), to produce one or more fluorinated alkanes, preferably one or more fluorinated propanes having a degree of fluorination of N+1; and dehydrofluorinating the fluorinated alkane to produce a crude
15 product stream comprising one or more of the desired fluorinated olefins having a degree of fluorination of N.

 In preferred applications, the present methods further comprise the step of providing a separation system capable of separating from the crude product stream a first of said desired fluorinated olefins and further providing at least a first and a
20 second alternative flow path for said first fluorinated olefin, said first flow path being adapted to introduce at least a portion of said first fluorinated olefin into said hydrogenation reaction step and said second flow path being adapted to deliver said first desired fluoroolefin to further processing to produce a relatively refined product stream containing said first desired fluoroolefin, said first and second alternate flow
25 paths being operable independently.

 In another aspect, the present invention provides systems capable of simultaneously and alternatively producing 1,1,1,2-tetrafluoropropene (HFO-1234yf) and 1,1,1,2,3-pentafluoropropene (HFO1225ye) comprising: (a) at least a first hydrogenation reactor adapted to be operated under conditions effective to produce
30 from a feed stream comprising HFP, HFO-1225ye, and combinations of these at least

one hydrogenation reaction product stream comprising in the alternative a major proportion of HFC-236ea or a major proportion of HFC-245ba, each on the basis of the total of HFC- 236ea and HFC-245ba in the hydrogenation reaction product stream; (b) at least one dehydrofluorination reactor adapted to be operated under conditions effective to produce from at least a portion of the hydrogenation reaction product at least one of 1,1,1,2-tetrafluoropropene (HFO-1234yf), 1,1,1,2,3-pentafluoropropene (HFO1225ye), and combinations of these. In preferred embodiments, the systems further comprise: (c) at least a first separator capable of separating said hydrogenation reactor product stream into at least a first stream relatively rich in HFC-236ea and at least a second stream relatively rich in HFC-245eb; and (d) at least a second separator capable of separating dehydrofluorination reaction product into at least a first stream relatively rich in HFO-1234yf and at least a second stream relatively rich in HFO-1225ye. In certain preferred embodiments the systems include a flow path for recycling at least a portion, and preferably all, of the stream rich in HFO-1225ye to the hydrogenation reactor and a flow path. In certain preferred embodiments, the systems include at least a second flow path operable simultaneously and independently of said first flow path to deliver said HFO-1225ye to further processing to produce a relatively refined product stream containing relatively higher concentrations of HFO-1225ye.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic process flow diagram according to one embodiment of the present invention.

FIG. 2 is a semi-schematic process flow diagram according to one embodiment of the hydrogenation step of the present invention.

DETAILED DESCRIPTION

In certain highly preferred embodiments, the desired fluorinated olefins of the present invention comprise one or more C2 to C6 fluoroalkenes, preferably compounds having a formula as follows:



where X^1 is a C1, C2, C3, C4, or C5 unsaturated, substituted or unsubstituted, alkyl radical, each R is independently Cl, F, Br, I or H, and z is 1 to 3. Highly preferred among such compounds are propenes and butenes having from 3 to 5 fluorine substituents, and among these tetrafluoropropenes (HFO-1234) and

5 pentafluoropropenes (HFO-1225) are especially preferred.

Preferred processes of the present invention comprise reacting a fluorinated olefin starting material with a degree of halogen substitution of N+1 having substantially the same number of carbon atoms as the fluorinated olefin(s) to be synthesized with a degree of halogen substitution of N. Preferably the fluorinated

10 olefin starting material having a degree of fluorine substitution of N + 1 is exposed to reaction conditions effective to produce a reaction product containing one or more fluorinated alkanes having the same number of carbons atoms as the olefin. In one preferred aspect of the present invention, this olefin conversion step comprises a reaction that is sometimes referred to herein for convenience, but not necessarily by

15 way of limitation, as a reduction or hydrogenation step. The fluorinated alkane is then preferably converted to a fluorinated olefin having a degree of fluorine substitution of N. In one preferred aspect of the present invention, this alkane conversion step comprises a reaction that is sometimes referred to herein for convenience, but not necessarily by way of limitation, as a dehydrohalogenation reaction or more

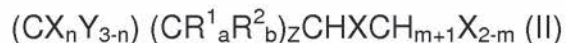
20 particularly in certain embodiments as a dehydrofluorination or dehydrochlorination reaction.

According to one aspect of the present invention, the present processes preferably comprise the steps of

(a) hydrogenating a compound of formula (I)



under conditions effective to form at least one fluorinated alkane of formula (II)



where:

each X is independently Cl, F, I or Br;

each Y is independently H, Cl, F, I or Br;

each R¹ is independently H, Cl, F, I, Br or unsubstituted or halogen substituted methyl or ethyl radical;

each R² is independently H, Cl, F, I, Br or unsubstituted or halogen substituted methyl or ethyl radical;

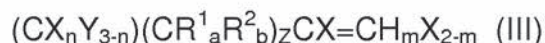
n is 1, 2 or 3;

a and b are each 1 or 2, provided that a+b = 2;

m is 0, 1 or 2; and

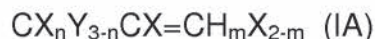
Z is 0, 1, 2 or 3, and

- 10 (b) dehydrohalogenating the compound of formula (II) under conditions effective to produce a fluoroolefin with a lower degree of fluorine substitution than the compound of formula (I), preferably to produce a compound of formula (III):



where each n is the same value as in formula (I) and m is 0 or 1.

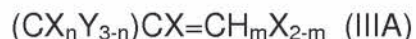
- 15 In certain preferred embodiments, the reactant of formula (I) comprises a three carbon olefin of formula (IA) wherein z is 0, namely



to produce a three carbon alkane of formula (IIA) as follows:



- 20 where X, Y, n, and m are all as indicated above, which compound is then dehydrohalogenated to form a compound of formula (IIIA)



where n is the same value as in formula (IA) and m is 0 or 1.

- 25 In certain highly preferred aspects of such embodiments, a saturated terminal carbon of the compounds of formulas (I) or (IA) is fully substituted with fluorine (for

example, n on the saturated terminal carbon is 3 and each X on that carbon is F), and even more preferably n is 3 and each X in the compound is F.

For three carbon embodiments of such preferred aspects, the compound of Formula (IA) is preferably a fluoropropene having from three to six fluorine substituents, and potentially other halogen substituents, including for example hexafluoropropene (that is, Z is 0, n is 3, m is 0, and all X are F) or pentafluoropropene (that is, Z is 0, n=3, m is 1, and all X are F), and the compound of formula (IIA) preferably comprises, and more preferably is selected from the group consisting of, one or more of the following fluorinated alkanes: chlorotrifluoropropane (HCFC-244) and pentafluoropropane (HFC-245), and hexafluoropropane (HFC-236), including all isomers of each of these, but preferably 1,1,1,2,3-pentafluoropropane (HFC-245eb), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and combinations of these. In certain preferred embodiments the fluorinated alkane produced by the conversion step has a degree of fluorine substitution of N+1.

In preferred embodiments, the step wherein the olefin is converted to an alkane is carried out under conditions effective to provide a formula (I) conversion of at least about 40%, more preferably at least about 55%, and even more preferably at least about 70%. In certain preferred embodiments the conversion is at least about 90%, and more preferably about 99%. Further in certain preferred embodiments, the conversion of the compound of formula (I) to produce a compound of formula (II) is conducted under conditions effective to provide a formula (II) selectivity of at least about 60%, more preferably at least about 80%, and more preferably at least about 90%, and even more preferably about 100%.

In preferred embodiments, the step wherein the alkane is converted to a fluorinated olefin having a degree of fluorination of N is carried out under conditions effective to provide a formula (II) conversion of at least about 40%, more preferably at least about 55%, and even more preferably at least about 70%. In certain preferred embodiments the conversion is at least about 90%, and more preferably about 95%. Further in certain preferred embodiments, the conversion of the compound of formula (II) to produce a compound of formula (III) is conducted under conditions effective to

provide a formula (III) selectivity of at least about 60%, more preferably at least about 80%, and more preferably at least about 90%, and even more preferably about 98%.

With reference now to Figure 1, the preferred methods and systems of the present invention comprise at least a first hydrogenation reactor A and at least a first feed stream 1 to the hydrogenation reactor which comprises at least one fluorinated olefin having a degree of halogen substitution, and preferably a degree of fluorine substitution, of $N+1$. The hydrogenation step A preferably involves also a feed stream 2 comprising a reducing agent. The converting step A preferably includes providing one or more reaction vessels, at least one of which preferably contains a reduction or hydrogenation catalyst, and introducing streams 1 and 2 into the vessel(s) under conditions effective to achieve the desired conversion.

Although the streams 1 and 2 in the figure are shown for convenience as being separate streams, this is done for convenience and the present invention is not so limited. For example, the streams 1 and 2 could in certain embodiments be combined outside the vessel and then introduced to the vessel together, or in other embodiments stream 1 and stream 2 might each comprise several separate streams, each of which is introduced into the vessel(s) at different times and/or at different locations. Furthermore, the present invention contemplates, as will be described in more detail hereinafter, that the stream 1 may actually comprise two or more separate streams and the step A may comprise two or more reaction vessels. All such variations are contemplated. This same convention has been used and applies herein throughout to all use of the term "stream," "step" and the like in both the description and in the figures, unless specifically indicated otherwise.

The preferred converting step A produces at least one reaction product stream 3 which contains a fluorinated alkane in accordance with the present invention. Stream 3 is preferably introduced to a separation step B which provides at least a first stream 5 which is used as a reactant in the dehydrohalogenation step C. A stream or flow path 4 is also preferably provided from separation step B for returning at least a portion of the reaction product stream 3 to the hydrogenation reaction step A. Stream 5, which contains at least a portion of the fluorinated alkane reaction product from step A, is fed to the dehydrohalogenation step C, wherein the fluorinated alkane in stream

5 is converted to a fluorinated olefin have a degree of halogen substitution, and in certain preferred embodiments fluorine substitution, of N in accordance with the present invention. The converting step C preferably includes providing one or more reaction vessels, at least one of which preferably contains a dehydrohalogenation catalyst and introducing at least stream 5 into the vessel(s) under conditions effective to produce the desired fluoroolefin in crude reaction product stream 6.

In preferred embodiments, the conversion step C produces a reaction product which includes not only one or more of the desired fluoroolefins, but also hydrogen and other by-products, which are withdrawn from the reaction step C by crude product stream 6. In such embodiments it is generally preferred to introduce the stream 6 into a separation step D in which at least a portion of the hydrogen is separated from the stream to produce at least a first stream 7 relatively rich (in comparison to the crude product stream 6) in the desired fluorinated olefin, at least a second stream relatively rich (in comparison to the feed stream 4) in hydrogen and/or other byproducts, and at least one recycle stream 8 for returning at least a certain portion of the unreacted reactants to the dehydrohalogenation step C. In addition, according to preferred embodiments, it is preferred to provide from the separation step or unit a flow path 10 for returning at least a portion of any HFO-1224ye contained in the crude reaction product 6 to the hydrogenation step A.

Preferred aspects of each of the steps A, B, C and D, and each of the feed streams, product streams and flow paths associated therewith are described below.

THE HYDROGENATION STEP

Although it is contemplated that the hydrogenation or reduction step may be conducted in batch operation, it is preferred that the hydrogenation reaction is carried out as a substantially continuous operation. Furthermore, it is contemplated that the hydrogenation reaction may be conducted in a single reaction vessel, it is also contemplated that reaction step A may comprise two or more reactors or reaction stages in parallel, in series, or both, or any combination of reactor designs. In addition, it is contemplated that the reaction step may include one or more feed preheating steps or stages, depending on the particulars of each application.

While it is possible that the reaction may involve in certain embodiments a liquid phase reaction, it is contemplated that in preferred embodiments the hydrogenation reaction comprises, and even more preferably consists of, at least one vapor phase reaction stage.

5 In one preferred embodiment of the present invention, the hydrogenation step comprises a reaction step A having associated therewith at least a first flow path or feed stream 1A, at least a second flow path or feed stream 1B and at least a third flow path or feed stream 2, with each flow path being independently operable. One such embodiment is illustrated schematically in Figure 2. In such embodiments, it is
10 preferred that the first flow path or feed stream 1A comprises HFP and preferably substantially all of the HFP being fed to the reaction step A, the second path or feed stream 1B comprises HFO-1225ye, and preferably substantially all of the HFO-1225ye being fed to the reaction step A (it being recognized that the feed stream 1B in many
15 embodiments will have a substantially zero flow and that in other embodiments this feed stream 1B may in fact be a recycle stream from subsequent operations in the process). The feed stream 2 comprises the hydrogenation agent, preferably H₂, for the reaction step A. Flow path or stream 4 is at path for allowing introduction of a recycle stream into the reaction step. In some embodiments, the actual flow of recycle
20 stream 4 is zero, but in preferred embodiments, the recycle stream comprises a relatively low temperature stream comprising a portion of the reaction product stream 3A after it has been cooled and separated, the content of recycle stream 4, when present, preferably being relatively rich in HFC-236ea, HFC-245eb, or a combination of these.

In another preferred embodiment of the present invention as illustrated in
25 Figure 3, the hydrogenation step comprises at least a first reaction step A1 and a second reaction step A2. The first reaction step A1, which may comprise one or more reaction stages in parallel or in series or a combination of parallel or series, having associated therewith at least a first flow path or feed stream 1A and at least a second flow path or feed stream 2A, with each flow path being independently operable. The
30 first reaction step A1, which may comprise one or more reaction stages in parallel or in series or a combination of parallel or series, having associated therewith at least a first

flow path or feed stream 1A and at least a second flow path or feed stream 2A, with each flow path being independently operable. In such embodiments, it is preferred that the first flow path or feed stream 1A comprises HFP and preferably substantially all of the HFP being fed to the reaction step A, the second path or feed stream 2B
5 comprises the hydrogenation agent, preferably H₂, for the reaction step A. Flow path or stream 4A is at path for allowing introduction of a recycle stream into the reaction step. In some embodiments, the actual flow of recycle stream 4A is substantially zero, but in preferred embodiments, the recycle stream comprises a relatively low temperature stream comprising a portion of the reaction product stream 3A after it has
10 been cooled and separated, the content of recycle stream 4, when present, preferably being relatively rich in HFC-236ea, HFC-245eb, or a combination of these. The first reaction step A1, which may comprise one or more reaction stages in parallel or in series or a combination of parallel or series, having associated therewith at least a first flow path or feed stream 1A and at least a second flow path or feed stream 2A, with
15 each flow path being independently operable.

In connection with the reaction stage converting HFP in the hydrogenation reactor, it is preferred in certain embodiments to use a trickle bed reactor. It is contemplated that the reaction in such case proceeds as follows:



20 A major side reaction is contemplated to be:



The second reaction step A2, which may comprise one or more reaction stages in parallel or in series or a combination of parallel or series, having associated therewith at least a first flow path or feed stream 1B and at least a second flow path
25 or feed stream 2B, with each flow path being independently operable. In such embodiments, it is preferred that the first flow path or feed stream 2B, when present, comprises HFO-1225ye, and preferably substantially all of the HFO-1225ye being fed to the reaction step A (it being recognized that the feed stream 2B in many embodiments will have a substantially zero flow and that in other embodiments this
30 feed stream 2B may in fact be a recycle stream from subsequent operations in the process). The second path or feed stream 2B comprises the hydrogenation agent,

preferably H₂, for the reaction step A2. Flow path or stream 4B is at path for allowing introduction of a recycle stream into the reaction step. In some embodiments, the actual flow of recycle stream 4B is zero, but in preferred embodiments, the recycle stream comprises a relatively low temperature stream comprising a portion of the reaction product stream 3A and/or 3B after it has been cooled and separated, the content of recycle stream 4B, when present, preferably being relatively rich in HFC-236ea, HFC-245eb, or a combination of these. Flow path or stream 10 is at path for allowing introduction of a second recycle stream into the reaction step, which in preferred embodiments comprises at least a portion of the reaction product stream 6 after being processed to comprise a stream relatively rich in HFO-1225ye.

In connection with the reaction stage converting HFO-1225ye in the hydrogenation reactor, it is preferred in certain embodiments to use a trickle bed reactor. It is contemplated that the reaction in such case proceeds as follows:



A major side reaction is contemplated to be:



Preferably, the hydrogenation reaction conditions are controlled in the reaction in order to achieve the desired conversion and/or selectivity in accordance with the present invention. As used herein, the term "reaction conditions" is intended to include the singular and means control of any one or more processing parameters, including possibly using or not using a reaction vessel or stage, which can be modified by the operator of the reaction to produce the conversion and/or selectivity of the feed material in accordance with the teachings contained herein. By way of example, but not by way of limitation, conversion of the feed material may be controlled or regulated by controlling or regulating any one or more of the following: the temperature of the reaction, the flow rate of the reactants, the presence of diluent, the amount of catalyst present in the reaction vessel, the shape and size of the reaction vessel, the pressure of the reaction, and any one combinations of these and other process parameters which will be available and known to those skilled in the art in view of the disclosure contained herein. The size and shape, and other characteristics of the reaction vessel itself may vary widely with the scope of the present invention, and it is contemplated

that the vessel associated with each stage may be different than or the same as the vessel associated with the upstream and downstream reaction stages. Furthermore, it is contemplated that all reaction stages can occur inside a single vessel, provided that means and mechanisms necessary to control conversion are provided. For example,
5 it may be desirable in certain embodiments to utilize a single tubular reactor for each reaction stage, providing conversion control by judicious selection of the amount and/or distribution of catalyst throughout the tubular reactor. In such a case, it is possible to further control the conversion in different sections of the same tubular reactor by controlling the amount of heat removed from or added to different sections
10 of the tubular reactor.

Those skilled in the art will be readily able to select the type of catalyst(s) used for the hydrogenation step of the present invention in view of the teachings contained herein. For example, it is preferred in certain embodiments that at least one, but preferably all, reaction stages utilize palladium catalyst, preferably 1% palladium on
15 carbon, either alone or in combination with other catalysts. In this regard one or more of the hydrogenation catalyst disclosed in US Patent 5, 679,875, which is incorporated herein by reference, maybe used for one or more of the reaction stages in accordance with the present invention. In certain preferred embodiments, the catalyst preferably comprises palladium supported on carbon, such as a carbon mesh.

Thus, certain embodiments of the present methods comprise bringing a fluorinated olefin in accordance with formula I and a hydrogenation agent, such as H₂, into contact with a first amount of catalyst in at least a first reaction stage to produce a reaction stream comprising hydrofluorocarbon(s), unreacted fluorinated olefin and hydrogen. In certain preferred embodiments the hydrogenation step is followed by a
20 preferred separation step as described below.

While it is contemplated that a wide variety of hydrogenation reaction temperatures may be used, depending on relevant factors such as the catalyst being used and the most desired reaction product, it is generally preferred that the reaction temperature for the hydrogenation step is from about 50°C to about 150°C, preferably
25 about from 75°C to about 115°C, and even more preferably from about 90°C to about 100°C.

In general it is also contemplated that a wide variety of reaction pressures may be used, depending again on relevant factors such as the specific catalyst being used and the most desired reaction product. The reaction pressure can be, for example, from about 100psig to about 300psig, preferably about from 150 psig to about 250 psig, and even more preferably about 200 psig.

Applicants have found, without being bound by or to any particular theory, that the use of a cooled recycle stream 4 in the hydrogenation reaction allows the feed materials to serve as a means for removing heat from the hydrogenation reaction. Since the reduction or hydrogenation reaction of the present invention is generally exothermic, and usually substantially exothermic, the use of such a recycle material has the effect in preferred embodiments of maintaining the reactor temperature below that which would exist if the recycle were not used, assuming all other process conditions were maintained the same.

It is contemplated that the amount of hydrogen used may vary widely. In preferred embodiments, the hydrogen is feed to the reaction step as a gas in a H₂:olefin feed ratio of from about 1:1 to about 2:1, and even more preferably ratio of from about 1:1 to about 1.5:1, and even more preferably about 1.3:1.

THE HYDROGENATION REACTION EFFLUENT SEPARATION

Thus, in certain preferred embodiments, the present invention includes the step of cooling at least a portion reactor product stream to remove at least a portion of the heat of reaction. In many preferred embodiments, this cooling step is included as part of the preferred aspects of the separation step B, which are described in connection with Figures 4, 5 and 6 below. Preferably the ratio of cooled recycled reaction product to fresh feed is about 12:1, with the temperature of the recycle stream preferably being at about 50C to about 100C, and even more preferably about 70C. In addition, in order to help remove heat of reaction, it is preferred in certain embodiments to introduce the fresh feeds and/or the recycle feeds to the reaction in the liquid phase and allowing the heat of reaction to evaporate the liquid feed and/or the reaction products and withdrawing the reaction products in the gas phase.

With reference now to Figure 4, the reaction product streams 3A and 3B are directed to a separation step B, which comprises in the embodiment of Figure 4 a cooling step B1 which produces one or more cooled reaction product streams 3AB, which in turn are fed to one or more separation stages B2. It is contemplated that those skilled in the art will be able to devise without undue experimentation many means and mechanisms for attaining such cooling in view of the teachings contained herein and all such means and mechanisms are with the scope of the present invention. The preferred separation step B2 preferably includes at least a first separation step which produces a first stream 4 relatively rich in unreacted hydrogen, fluorinated alkane, such as HFC-236ea and/or HFC-245eb, or a combination of these, which may be recycled, with or without further processing, to the reaction step A. A second stream 5, which is relatively rich in the fluorinated alkane, such as HFC-236ea, HFC-245eb, is also produced from the separation step B2.

In one preferred embodiment shown in Figure 4A, the separation step comprises, in addition to the cooling step B1 and the separation step B2 which produces at least a first cooled stream 4A containing a portion of the reaction product, which is preferably recycled to the reaction step A, and a crude product stream 100 which is fed to a further separation step B3 in which a substantial portion of excess hydrogen in the stream 100 is purged from the stream and sent for disposal or further processing in stream 4B. The stream 101 from the separation step B3 is then feed to a further separation step B4 where unwanted by products are removed in stream 4C and one or more product streams 5A and 5B are produced. In preferred embodiments, stream 5A is relatively rich in a first fluorinated alkane, preferably HFC-236ea, and a second stream 5B rich in a second fluorinated alkane, preferably HFC-245eb.

In another embodiment described with reference now to Figure 5, the reaction product streams 3A and 3B are each directed to a separate separation steps, which comprise separate cooling steps B1 and B1', each of which produces one or more cooled reaction product streams 3A' and 3B', which in turn are fed to separate separation stages B2 and B2' to produce a first stream 5A relatively rich in a first of the fluorinated alkane products, such as HFC-236ea when the feed stream 3A is rich

in HFP, and a second reaction product stream 5B relatively rich in a second of the fluorinated alkane products, such as HFC-245ba when the feed stream 3B is rich in HFO-1225ye. A stream 4 (not shown) as described above in connection with Figure 4 may also be removed from each of the steps B2 and B2'. In addition, the particular
5 embodiments shown and described in Figure 4A may also be adapted for use in connection with one or both the separation steps B and B' shown in Figure 5.

DEHYDROHALOGENATION

It is contemplated that the dehydrohalogenation reaction step may be
10 preformed using a wide variety of process parameters and process conditions in view of the overall teachings contained herein, such as for example it is contemplated that the dehydrohalogenation step may comprise, in certain nonpreferred embodiments, a liquid phase reaction. However, it is preferred in many embodiments of the present invention that this reaction step comprise a gas phase reaction, preferably in the
15 presence of catalyst, preferably a metal catalyst, and even more preferably one or more transition metal-based catalysts (including in certain preferred embodiments transition metal halide catalysts), such as FeCl_3 , chromiumoxyfluoride, Ni (including Ni mesh), NiCl_2 , CrF_3 , and mixtures thereof, supported or in bulk. Other catalysts include carbon-supported catalysts, antimony-based catalysts (such as SbCl_5),
20 aluminum-based catalyst (such as AlF_3 , Al_2O_3 , and fluorinated Al_2O_3). It is expected that many other catalysts may be used depending on the requirements of particular embodiments, including for example palladium-based catalyst, platinum-based catalysts, rhodium-based catalysts and ruthenium-based catalysts. Of course, two or more any of these catalysts, or other catalysts not named here, may be used in
25 combination.

In general it is preferred that the catalysts are fluorinated. In preferred embodiments, fluorination of the catalysts comprises exposing the catalyst to a stream of HF at about reaction temperature and pressure. The gas phase dehydrohalogenation reaction may be conducted, for example, by introducing a
30 gaseous form of a compound of formula (II) into a suitable reaction vessel or reactor. Preferably the vessel is comprised of materials which are resistant to corrosion as

Hastelloy, Inconel, Monel and/or fluoropolymers linings. Preferably the vessel contains catalyst, for example a fixed or fluid catalyst bed, packed with a suitable dehydrohalogenation catalyst, with suitable means to heat the reaction mixture to the desired reaction temperature.

5 While it is contemplated that a wide variety of reaction temperatures may be used, depending on relevant factors such as the catalyst being used and the most desired reaction product, it is generally preferred that the reaction temperature for the dehydrohalogenation step is from about 150 °C to about 600 °C, preferably about from 200 °C to about 300 °C, and even more preferably from about 240 °C to about 260 °C.

10 In general it is also contemplated that a wide variety of reaction pressures may be used, depending again on relevant factors such as the specific catalyst being used and the most desired reaction product. The reaction pressure can be, for example, superatmospheric, atmospheric or under vacuum.

15 In certain embodiments, an inert diluent gas and/or an oxidizing agent, such as nitrogen, oxygen and mixture of nitrogen and oxygen, may be used in combination with the compound of formula (II) as a feed to the dehydrohalogenation step. When such a diluent and/or oxidizing agent is used, it is generally preferred that the feed stream comprise formula (II) compound in an amount of from about 5% to greater than 95% by weight based on the combined weight of diluent and formula (II)
20 compound.

 It is contemplated that the amount of catalyst used will vary depending on the particular parameters present in each embodiment. In preferred embodiments, the contact time, which is expressed as the ratio of the volume of the catalyst (ml) to the total feed flow (ml/sec) is from about 0.1 seconds to about 1000 seconds, and
25 preferably from about 2 seconds to about 120 seconds.

 In general it is contemplated that the reaction is endothermic. To assist thermal management, it is contemplated in certain embodiments that the reactor comprises an isothermal tubular reactor, with heat input being provided by means of a relatively high temperature heating medium, such as hot salt and/or oil,
30 superheated steam, or re-circulating hot gas. In addition, recycling of the HFO-1225ye produced in the reaction may be used to help control the temperature of the

reaction.

One preferred dehydrohalogenation reaction comprises a dehydrofluorination reaction. For example, for embodiments in which the desired product of formula (III) is HFO-1234yf, it is preferred in certain embodiments that the compound of formula
5 (II) comprises 1,1,1,2,3 pentafluoropropane. Applicants have found that in such embodiments it is preferred to use as the catalyst a fluorinated chromium oxide catalyst.

Preferably in such dehydrofluorination embodiments, the conversion is at least about 50%, more preferably at least about 65%, and even more preferably at least
10 about 90%. Preferably, the selectivity to HFO-1234yf is at least about 70%, more preferably at least about 80% and more preferably at least about 90%.

Preferably before each cycle of use, the dehydrohalogenation catalyst is dried, pre-treated and activated. It may also be advantageous in certain embodiments to periodically regenerate the catalyst after prolonged use while in place in the reactor.
15 Pre-treatment may include heating the catalyst to about 250 °C to about 430 °C with a stream of nitrogen or other inert gas. The catalyst may then be activated by treating it with a stream of HF diluted with a large excess of nitrogen gas in order to obtain high catalyst activity. Regeneration of the catalyst may be accomplished by any means known in the art such as, for example, by passing air or oxygen over the catalyst at
20 temperatures of from about 100 °C to about 400 °C for from about 1 hour to about 3 days depending on the size of the reactor.

While it is possible that the reaction may involve in certain embodiments a liquid phase reaction, it is contemplated that in preferred embodiments the dehydrohalogenation reaction comprises, and even more preferably consists of, at
25 least one vapor phase reaction stage.

In one preferred embodiment of the present invention, the dehydrohalogenation step comprises a reaction step C having associated therewith at least a first flow path or feed stream 5A, at least a second flow path or feed stream 5B and at least a third flow path or feed stream 8, with each flow path being independently operable. One
30 such embodiment is illustrated schematically in Figure 6. In such embodiments, it is preferred that the first flow path or feed stream 5A comprises HFO-236ea and

preferably substantially all of the HFO-236ea being fed to the reaction step C, the second path or feed stream 5B comprises HFC-245ba, and preferably substantially all of the HFO-245ba being fed to the reaction step C (it being recognized that the feed stream 5B in many embodiments will have a substantially zero flow). Flow path or stream 8 is at path for allowing introduction of a recycle stream into the reaction step. In some embodiments, the actual flow of recycle stream 8 is zero, but in preferred embodiments, the recycle stream comprises a relatively low temperature stream comprising a portion of the reaction product stream 6A after it has been cooled and separated, the content of recycle stream 4, when present, preferably being relatively rich in HFC-236ea, HFC-245eb, or a combination of these.

In another preferred embodiment of the present invention as illustrated in Figure 7, the dehydrohalogenation step comprises at least a first reaction step C1 and a second reaction step C2. The first reaction step C1, which may comprise one or more reaction stages in parallel or in series or a combination of parallel or series, having associated therewith at least a first flow path or feed stream 5A and at least a second flow path or feed stream 8A, with each flow path being independently operable. The second reaction step C1, which may comprise one or more reaction stages in parallel or in series or a combination of parallel or series, having associated therewith at least a first flow path or feed stream 5B and at least a second flow path or feed stream 5B, with each flow path being independently operable. In such embodiments, it is preferred that the first flow path or feed stream 5A comprises HFO-236ea and preferably substantially all of the HFO-236ea being fed to the reaction step C, the second path or feed stream 5B comprises, when present, HFO-245eb and preferably substantially all of the HFO-245eb being fed to the reaction step C. Flow path or streams 8A and 8B are flow paths for allowing introduction of a recycle stream comprising at least a portion of unreacted feed back into the reaction step. In some embodiments, the actual flow of recycle streams 8A and 8B are substantially zero, but in preferred embodiments, the recycle streams comprises relatively low temperature streams comprising a portion of the reaction product streams 6A and 6B after they have been cooled and separated.

In connection with the reaction stage converting HFO-236ea in the dehydrogenation reactor, it is contemplated that the reaction in such case proceeds as follows:



5 It will be appreciated that the present processes may include an isomerization step to convert to a desirable isomer of HFO-1225ye, which would typically be carried out at temperatures of about 150C.

The second reaction step C2, which may comprise one or more reaction stages in parallel or in series or a combination of parallel or series, having associated
10 therewith at least a first flow path or feed stream 5B and at least a second flow path or feed stream 8B, with each flow path being independently operable. In such embodiments, it is preferred that the first flow path or feed stream 5B comprises HFC-245ba, and preferably substantially all of the HFC-245ba being fed to the reaction step C. The second path or feed stream 8B comprises recycle of a portion of the reaction
15 product, as described above.

In connection with the reaction stage converting HFC-245ba in the dehydrohalogenation reactor, it is contemplated that the reaction in such case proceeds as follows:



20 Preferably, the reaction conditions are controlled in the reaction in order to achieve the desired conversion and/or selectivity in accordance with the present invention. As used herein, the term "reaction conditions" is intended to include the singular and means control of any one or more processing parameters, including possibly using or not using a reaction vessel or stage, which can be modified by the
25 operator of the reaction to produce the conversion and/or selectivity of the feed material in accordance with the teachings contained herein. By way of example, but not by way of limitation, conversion of the feed material may be controlled or regulated by controlling or regulating any one or more of the following: the temperature of the reaction, the flow rate of the reactants, the presence of diluent, the amount of catalyst
30 present in the reaction vessel, the shape and size of the reaction vessel, the pressure of the reaction, and any one combinations of these and other process parameters

which will be available and known to those skilled in the art in view of the disclosure contained herein. The size and shape, and other characteristics of the reaction vessel itself may vary widely with the scope of the present invention, and it is contemplated that the vessel associated with each stage may be different than or the same as the vessel associated with the upstream and downstream reaction stages. Furthermore, it is contemplated that all reaction stages can occur inside a single vessel, provided that means and mechanisms necessary to control conversion are provided. For example, it may be desirable in certain embodiments to utilize a single tubular reactor for each reaction stage, providing conversion control by judicious selection of the amount and/or distribution of catalyst throughout the tubular reactor. In such a case, it is possible to further control the conversion in different sections of the same tubular reactor by controlling the amount of heat removed from or added to different sections of the tubular reactor.

THE DEHYDROHALOGENATION EFFLUENT SEPARATION

As mentioned above, in addition to producing a fluorinated olefin, preferably fluorinated propene, the dehydrofluorination reaction also produces HF. In one preferred embodiment, HF is removed from the dehydrofluorination product stream by countercurrent extraction with sulfuric acid. In this embodiment, the product stream containing the HF is fed in one direction to a column, preferably a packed column. At the same time, a stream of sulfuric acid is fed, preferably countercurrently, to the same packed column. Appropriate column packing is readily determinable by one skilled in the art. Suitable column packing materials include those made of non-metallic polymeric materials, metals and alloys that are not reactive in the presence of HF or sulfuric acid, such as PTFE, PFA, hastelloy, monel, and noble metals. Preferably, the stream of sulfuric acid contains from about 50% to about 100% sulfuric acid, and more preferably about 80% sulfuric acid. In one embodiment, the stream of sulfuric acid is continuously fed to the top of the packed column at a feed rate of about twice the feed rate of the product stream, which in preferred embodiments is fed from the bottom of the packed column and moves in an generally

upward direction substantially counter currently to the substantially down flowing stream containing the sulfuric acid. In certain embodiments, a stream comprising sulfuric acid and HF is removed from the bottom of the column and preferably at least a portion of the stream, and most preferably substantially all of the stream, is recycled
5 back to the extraction tower. The recycling step is repeated preferably until the HF concentration in the column bottom is greater than about 10 % by weight HF.

In one embodiment, the sulfuric acid and HF mixture containing greater than about 10% by weight HF is charged into a separate vessel. The mixture is then heated to a temperature sufficient to vaporize and flash off HF, which is collected.

10 Another embodiment includes purifying the HF collected from the flash distillation.

Optionally, the HF or HCl generated from the dehydrohalogenation reaction is scrubbed from the product stream using water or caustic solutions.

In certain preferred embodiments, the present invention includes the step of cooling at least a portion reactor product stream to remove at least a portion of the
15 heat of reaction. In many preferred embodiments, this cooling step is included as part of the preferred aspects of the separation step B, which are described in connection with Figures 4, 5 and 6 below. Preferably the ratio of cooled recycled reaction product to fresh feed is about 12:1, with the temperature of the recycle stream preferably being at about 50C to about 100C, and even more preferably about 70C. In addition, in
20 order to help remove heat of reaction, it is preferred in certain embodiments to introduce the fresh feeds and/or the recycle feeds to the reaction in the liquid phase and allowing the heat of reaction to evaporate the liquid feed and/or the reaction products and withdrawing the reaction products in the gas phase.

With reference now to Figure 8, the reaction product streams 6A and 6B are
25 directed to a separation step D, which comprises in the embodiment of Figure 8 a cooling step D1 which produces one or more cooled reaction product streams 7AB, which in turn are fed to one or more separation stages D2. It is contemplated that those skilled in the art will be able to devise without undue experimentation many means and mechanisms for attaining such cooling in view of the teachings contained
30 herein and all such means and mechanisms are with the scope of the present invention. The preferred separation step D2 preferably includes at least a first

separation step which produces a first stream 8 relatively rich in unreacted fluorinated alkane, such as HFC-236ea and/or HFC-245eb, or a combination of these, which may be recycled, with or without further processing, to the reaction step C.

5 In one preferred embodiment shown in Figure 8, the reaction product 7AB is separation step comprises a step for recovering any HF, preferably as described above, and a step for separating from the crude product stream unwanted by product to produce a relatively purified product stream rich in HFO-1234yf, HFO-1225ye, or a separate stream rich in both. In certain embodiments, a portion of the HFO-1225ye may be separated from the product stream and recycled back to the hydrogenation
10 reaction step and used as a feed thereto.

In an alternative embodiment, as illustrated in Figure 9, separate separation trains may be used for the effluent from the dehydrohalogenation reaction step, especially when the feeds HFC-236ea and HFC-245ba are feed substantially separately into separate reaction trains.

What is claimed is:

1. A process for the production of fluorinated olefins comprising the steps of:
 - (a) providing at least a first hydrogenation reaction vessel;
 - (b) introducing into said first hydrogenation reaction vessel at least a first hydrogenation feed stream comprising at least one fluorinated olefin feed selected from the group consisting of hexafluoropropene, 1,1,1,2,3-tetrafluoropropene (HFO-1225ye), and combinations of these;
 - (c) reacting said at least one fluorinated olefin from said first hydrogenation feed stream in said first hydrogenation reaction vessel with hydrogen to produce at least one fluorinated propane and at least one hydrofluorocarbon byproduct, said fluorinated propane being selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFO-236ea), 1,1,1,2,3-pentafluoropropane (HFO-245eb), and combinations of these,
 - (d) removing from said reaction vessel at least a first hydrogenation effluent stream comprising at least a portion of said at least one fluorinated propane, at least a portion of said at least one hydrofluorocarbon byproduct, and unreacted hydrogen;
 - (e) separating from said first hydrogenation effluent stream at least a substantial portion of said at least one hydrofluorocarbon byproduct contained therein and at least a substantial portion of said unreacted hydrogen contained therein to produce at least a first dehydrofluorination reaction feed stream comprising at least a substantial portion of said at least one fluorinated propane;
 - (f) providing at least a first dehydrofluorination reaction vessel containing at least fluorinated chromium oxide catalyst;
 - (g) introducing at least a portion of said first dehydrofluorination reaction feed stream into said first dehydrofluorination reaction vessel;
 - (h) reacting at least a substantial portion of said at least one fluorinated propane from said first dehydrofluorination reaction feed stream in said first

- dehydrofluorination reaction vessel to produce at least one dehydrofluorination effluent stream comprising at least one fluorinated olefin product and hydrogen fluoride, said at least one fluorinated olefin product being selected from the group consisting of 1,1,1,2-tetrafluoropropene (HFO-1234yf), 1,1,1,2,3-pentafluoropropene (HFO1225ye), and combinations of these; and
- (i) separating from said first dehydrofluorination effluent stream at least a substantial portion of said hydrogen fluoride to produce at least one fluorinated olefin product stream comprising a substantial portion of at least one of said fluorinated olefin products.
2. A process for the production of fluorinated olefins comprising the steps of:
- (a) providing at least a first hydrogenation reaction vessel containing palladium on carbon catalyst ;
- (b) introducing into said first hydrogenation reaction vessel at least a first hydrogenation feed stream comprising at least one fluorinated olefin feed selected from the group consisting of hexafluoropropene, 1,1,1,2,3-tetrafluoropropene (HFO-1225ye), and combinations of these;
- (c) reacting in said first hydrogenation reaction vessel at least one of said fluorinated olefins from said first hydrogenation feed stream with hydrogen to produce at least one fluorinated propane and at least one hydrofluorocarbon byproduct, said fluorinated propane being selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,2,3-pentafluoropropane (HFO-245eb), and combinations of these, said reaction being conducted at least in part at a temperature of from about 80 C to about 115 C and at a pressure of from about 150 psig to about 250 psig;
- (d) removing from said reaction vessel at least a first hydrogenation effluent stream comprising at least a portion of said at least one fluorinated propane,

at least a portion of said at least one hydrofluorocarbon byproduct, and unreacted hydrogen;

(e) separating from said first hydrogenation effluent stream at least a substantial portion of said at least one hydrofluorocarbon byproduct contained therein and at least a substantial portion of said unreacted hydrogen contained therein to produce at least a first dehydrofluorination reaction feed stream comprising at least a substantial portion of said at least one fluorinated propane;

(f) providing at least a first dehydrofluorination reaction vessel containing at least fluorinated chromium oxide catalyst;

(g) introducing at least a portion of said first dehydrofluorination reaction feed stream into said first dehydrofluorination reaction vessel;

(h) reacting at least a substantial portion of said at least one fluorinated propane from said first dehydrofluorination reaction feed stream in said first dehydrofluorination reaction vessel to produce at least one dehydrofluorination effluent stream comprising at least one fluorinated olefin product and hydrogen fluoride, said at least one fluorinated olefin product being selected from the group consisting of 1,1,1,2-tetrafluoropropene (HFO-1234yf), 1,1,1,2,3-pentafluoropropene (HFO-1225ye), said reacting step (g) being conducted at a temperature of from about 200C to about 300C and at a pressure of from about atmospheric to about 30 psig;

(i) separating from said first dehydrofluorination effluent stream at least a substantial portion of said hydrogen fluoride to produce at least one fluorinated olefin product stream comprising a substantial portion of at least one of said fluorinated olefin products; and

(j) when 1,1,1,2,3-pentafluoropropene (HFO-1225ye) is present in a substantial proportion in said at least one fluorinated olefin product stream, providing at least one flow path for introducing at least a substantial portion of

said 1,1,1,2,3-pentafluoropropene (HFO-1225ye) into said at least first hydrogenation reaction vessel.

3. A process for the production of fluorinated olefins comprising the steps of:
- (a) reacting at least a first hydrogenation feed stream comprising at least one fluorinated olefin feed selected from the group consisting of hexafluoropropene, 1,1,1,2,3-tetrafluoropropene (HFO-1225ye), and combinations of these with hydrogenating agent to produce at least one reaction product stream comprising fluorinated propane and at least one hydrofluorocarbon byproduct, said fluorinated propane being selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFO-236ea), 1,1,1,2,3-pentafluoropropane (HFO-245eb), and combinations of these,
 - (b) forming from said reaction product stream at least one stream relatively rich in at least one of said fluorinated propanes;
 - (c) dehydrofluorinating at least one stream relatively rich in at least one of said fluorinated propanes to produce at least one dehydrofluorination effluent stream comprising at least one fluorinated olefin product selected from the group consisting of 1,1,1,2-tetrafluoropropene (HFO-1234yf), 1,1,1,2,3-pentafluoropropene (HFO-1225ye), and combinations of these; and
 - (i) separating from said dehydrofluorination effluent stream at least a substantial portion of at least one of said fluorinated olefin products and recycling at least a portion of said fluorinated olefin product to said reaction step (a).

ABSTRACT

A process for the production of fluorinated olefins, preferably fluorinated propenes, by contacting a feed stream containing a fluorinated olefin and hydrogen with a first amount of catalyst to produce the hydrofluorocarbon, wherein a first exit stream contains unreacted fluorinated olefin and hydrogen; contacting the first exit stream with a second amount of catalyst to produce a hydrofluorocarbons, and contacting the hydrofluorocarbon with a catalyst for dehydrohalogenation to produce a product stream of fluorinated olefin.

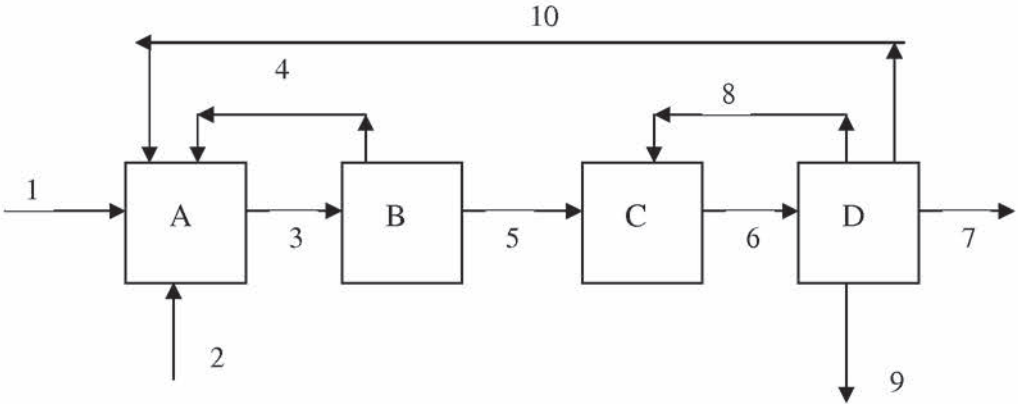


FIGURE 1

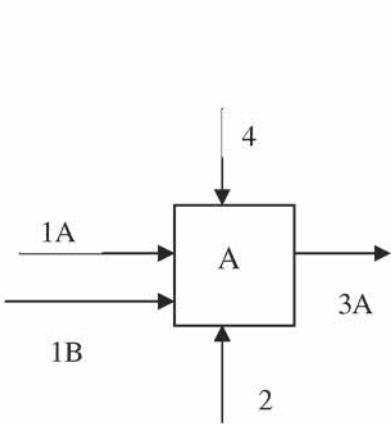


FIGURE 2

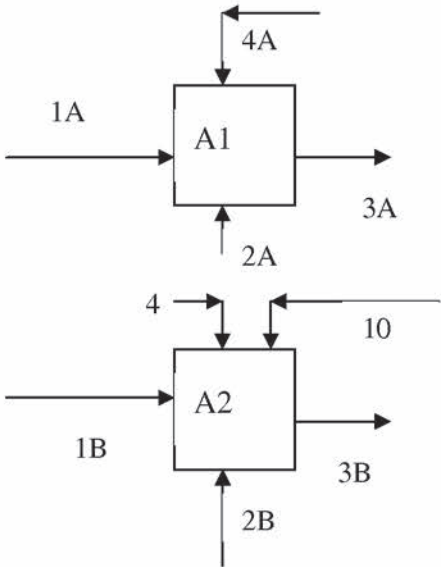


FIGURE 3

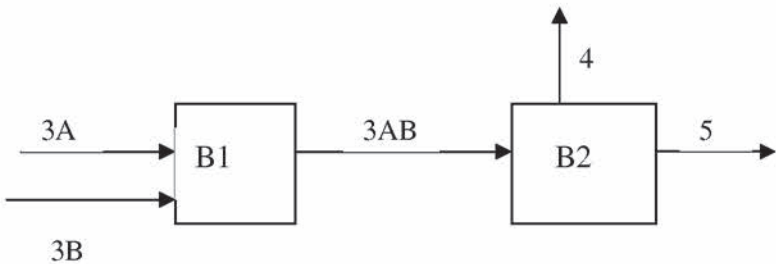


FIGURE 4

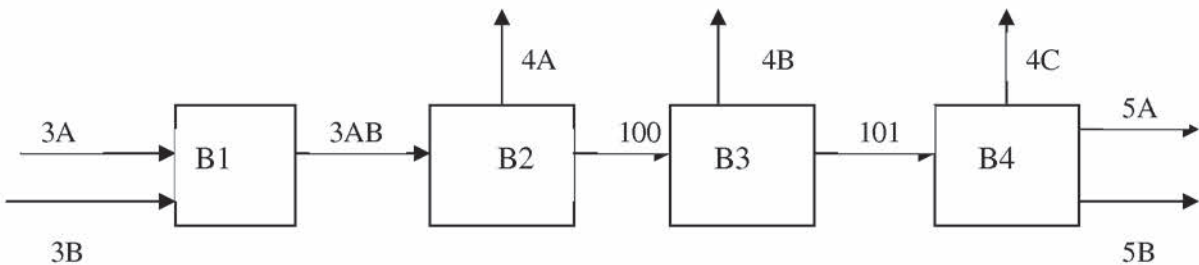


FIGURE 4A

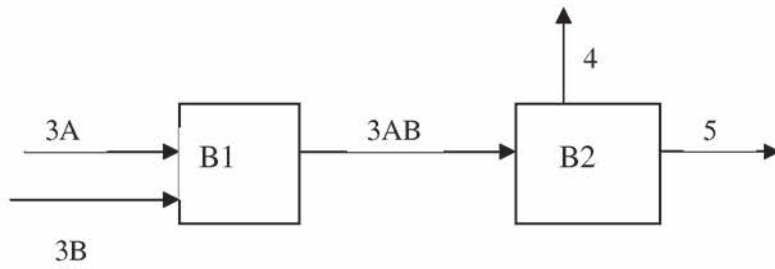


FIGURE 4

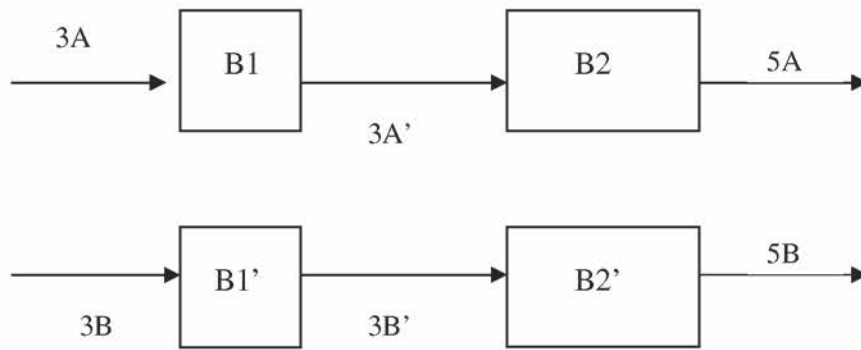


FIGURE 5

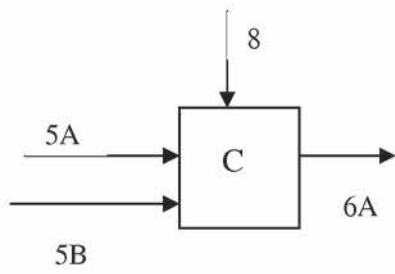


FIGURE 6

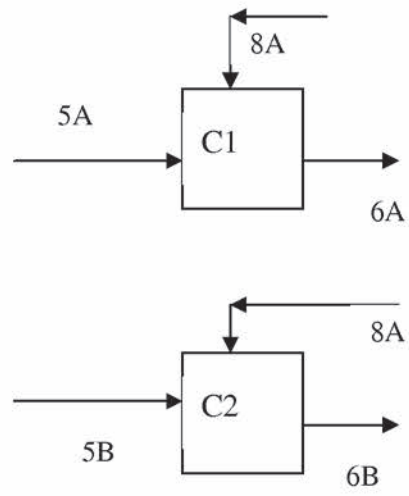


FIGURE 7

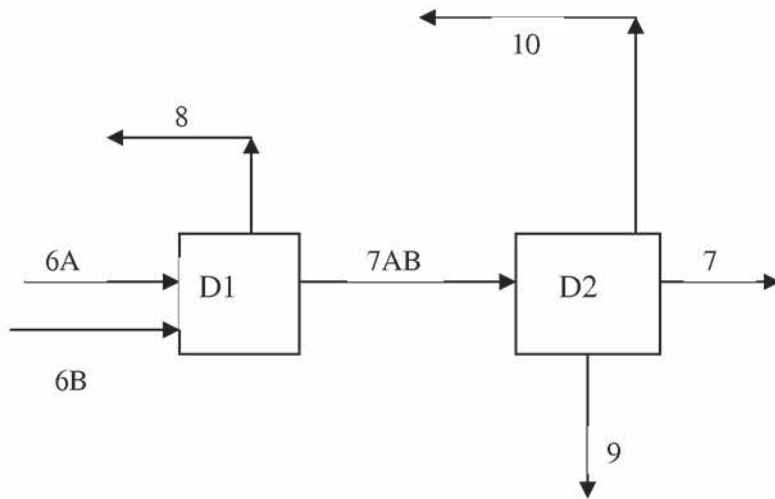


FIGURE 8

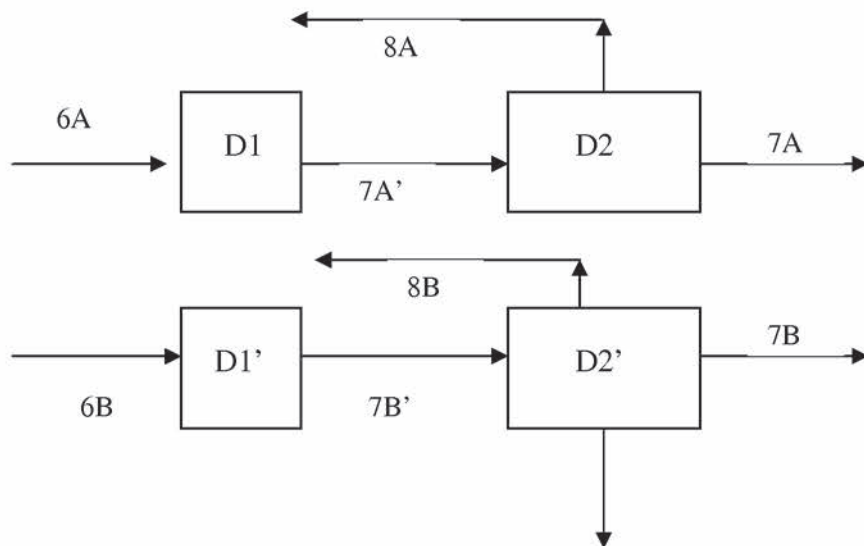


FIGURE 9

PATENT

Attorney Docket No.H0016235-4511

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Yuon Chiu

Stephen A. Cottrell

HsuehSung Tung

Application No.: **N/A**

Filing Date: **Herewith**

For: **Process of Co-Producing HFC-1225ye
and HFC-1234yf via 4-step reactions**

Group Art Unit: **N/A**

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**APPLICATION DATA SHEET
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Total Drawing Sheets::	N/A
Small Entity::	No
Petition included?::	No
Secrecy Order in Parent Appl.?::	No

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PATENT

Attorney Docket No.H0016235-4511

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Signature of Representative,

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Electronic Patent Application Fee Transmittal

Application Number:				
Filing Date:				
Title of Invention:	Process for the Manufacture of Fluorinated Olefins			
First Named Inventor/Applicant Name:	Yuon Chiu			
Filer:	Joseph F. Posillico/Fariha Ahmed			
Attorney Docket Number:	H0016235-4511			
Filed as Large Entity				
Provisional Filing Fees				
Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Basic Filing:				
Provisional application filing	1005	1	210	210
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD(\$)
Miscellaneous:				
Total in USD (\$)				210

Electronic Acknowledgement Receipt

EFS ID:	2999968
Application Number:	61036526
International Application Number:	
Confirmation Number:	4815
Title of Invention:	Process for the Manufacture of Fluorinated Olefins
First Named Inventor/Applicant Name:	Yuon Chiu
Customer Number:	00128
Filer:	Joseph F. Posillico/Fariha Ahmed
Filer Authorized By:	Joseph F. Posillico
Attorney Docket Number:	H0016235-4511
Receipt Date:	14-MAR-2008
Filing Date:	
Time Stamp:	12:46:11
Application Type:	Provisional

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	\$210
RAM confirmation Number	7497
Deposit Account	195425
Authorized User	BARRON,ALEXIS

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Charge any Additional Fees required under 37 C.F.R. Section 1.21 (Miscellaneous fees and charges)

File Listing:					
Document Number	Document Description	File Name	File Size(Bytes) /Message Digest	Multi Part /.zip	Pages (if appl.)
1		H0016235_35401_As_filed.pdf	155648	yes	34
			5bf7892fbd005252ca1954a092610268d59484fd		
	Multipart Description/PDF files in .zip description				
	Document Description		Start	End	
	Specification		1	23	
	Claims		24	27	
	Abstract		28	28	
	Drawings-only black and white line drawings		29	34	
Warnings:					
Information:					
2	Application Data Sheet	35401USA_ADS_H0016235.pdf	77625	no	4
			ec6101ef06b7297fc618f6d6555219c0ac8cec1		
Warnings:					
Information:					
This is not an USPTO supplied ADS fillable form					
3	Fee Worksheet (PTO-06)	fee-info.pdf	8123	no	2
			af1cd94dc0a49a75dd4d62f1e6d18c62b111f6b		
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Total Files Size (in bytes):			241396		

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.