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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	H0024680-4511
	Application Number	
Title of Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS	

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Applicant 1 Remove

Applicant Authority	◉ Inventor	○ Legal Representative under 35 U.S.C. 117	○ Party of Interest under 35 U.S.C. 118

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Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Williamsville	State/Province	NY	Country of Residence i	US

Citizenship under 37 CFR 1.41(b) i	BA

Mailing Address of Applicant:

Address 1	770 Maple Road, Apt. 9B
Address 2	

City	Williamsville	State/Province	NY
Postal Code	14221	Country i	US

Applicant 2 Remove

Applicant Authority	◉ Inventor	○ Legal Representative under 35 U.S.C. 117	○ Party of Interest under 35 U.S.C. 118

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	HSUEH	SUNG	TUNG	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Getzville	State/Province	NY	Country of Residence i	US

Citizenship under 37 CFR 1.41(b) i	US

Mailing Address of Applicant:

Address 1	16 Vassar Drive
Address 2	

City	Getzville	State/Province	NY
Postal Code	14068	Country i	US

Applicant 3 Remove

Applicant Authority	◉ Inventor	○ Legal Representative under 35 U.S.C. 117	○ Party of Interest under 35 U.S.C. 118

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	HALUK		KOPKALLI	

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City	Staten Island	State/Province	NY	Country of Residence i	US

Pet'rs Exhibit 1015
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Title of Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS	

Citizenship under 37 CFR 1.41(b) i	US			
Mailing Address of Applicant:				
Address 1	364 Giffords Lane			
Address 2				
City	Staten Island	**State/Province**	NY	
Postal Code	10308	**Country**i	US	

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

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☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	91970		
Email Address	patentservices-us@honeywell.com	Add Email	Remove Email

Application Information:

Title of the Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS		
Attorney Docket Number	H0024680-4511	**Small Entity Status Claimed**	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Suggested Class (if any)		**Sub Class (if any)**	
Suggested Technology Center (if any)			
Total Number of Drawing Sheets (if any)	3	**Suggested Figure for Publication (if any)**	

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☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	H0024680-4511
	Application Number	
Title of Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS	

Customer Number	91970

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This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this information in the application data sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78(a)(2) or CFR 1.78(a)(4), and need not otherwise be made part of the specification.

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
	non provisional of	61392242	2010-10-12
Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
	Continuation in part of	13195429	2011-08-01
Prior Application Status	Patented		Remove

Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)	Patent Number	Issue Date (YYYY-MM-DD)
13195429	Continuation in part of	12402372	2009-03-11	8013194	2011-09-06

Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
12402372	non provisional of	61036526	2008-03-14

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Application Number	Country [i]	Parent Filing Date (YYYY-MM-DD)	Priority Claimed
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Organization Name	HONEYWELL INTERNATIONAL INC.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	H0024680-4511
	Application Number	
Title of Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS	

Mailing Address Information:			
Address 1	101 Columbia Road		
Address 2			
City	Morristown	**State/Province**	NJ
Country [i]	US	Postal Code	07962
Phone Number	973-455-2062	Fax Number	973-455-5904
Email Address	patentservices-us@honeywell.com		
Additional Assignee Data may be generated within this form by selecting the **Add** button.		Add	

Signature:

A signature of the applicant or representative is required in accordance with 37 CFR 1.33 and 10.18. Please see 37 CFR 1.4(d) for the form of the signature.					
Signature	/J. Eric Sumner/			Date (YYYY-MM-DD)	2011-09-09
First Name	John	Last Name	Sumner	Registration Number	58699

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INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is related to and claims the priority benefit of United States provisional application number 61/392,242 filed October 12, 2010, the contents of which are incorporated herein by reference.

[0002] This application is also a continuation-in-part of United States application serial number 13/195,429, filed August 1, 2011, which is a continuation of U.S. Patent Application No. 12/402,372, filed March 11, 2009 (now U.S. Patent No. 8,013,194), which in turn claims priority benefit of US Provisional Patent Application No. 61/036,526, filed March 14, 2008, each of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0003] The present invention relates to processes for producing haloalkenes, particularly, though not exclusively, 2,3,3,3-tetrafluoropropane (HFO-1234yf) and/or 1,2,3,3,3-pentafluoropropene (HFO-1225ye).

BACKGROUND OF THE INVENTION

[0004] Chlorine-containing compounds, such as chlorofluorocarbons (CFCs), have been employed as refrigerants, foam blowing agents, cleaning agents, solvents, heat transfer media, sterilants, aerosol propellants, dielectrics, fire extinguishing agents, and power cycle working fluids. Such chlorine-containing compounds have proven to be detrimental to the Earth's ozone layer. Many of the hydrofluorocarbons (HFCs), used as the substitutes of CFCs, have been found

to contribute to global warming. For these reasons, there is a worldwide effort to develop new compounds that are more environmentally benign while at the same time being as effective, or more effective, from a performance standpoint.

[0005] Applicants have come to appreciate that 1,1,1,2,3-pentafluoropropene (HFO-1225ye) and 1,1,1,2-tetrafluoropropene (HFO-1234yf) are each useful in one or more of the above mentioned applications. Accordingly, compositions containing either or both fluorinated olefins are among the materials being developed for such use.

[0006] Methods for producing HFO-1234yf and HFO-1225ye are known. In one example, it is known that hexafluoropropylene (HFP) can be hydrogenated to produce 1,1,1,2,3,3-hexafluoropropane (HFC-236ea). HFC-236ea is then used as a reactant in a dehydrogenation reaction to produce HFO-1225ye. It is further known that HFO-1225ye can be hydrogenated to produce 1,1,1,2,3-pentafluoropropane (HFC-245eb) and that HFC-245eb can then be dehydrofluorinated to produce HFO-1234yf.

[0007] U.S. Patent Application Publication No. 2009/0234165, the contents of which are incorporated by reference herein, further provides that HFO-1225ye and HFO-1234yf can be produced in a single facility. Most notably, it was realized that the hydrogenation of HFP can yield both HFC-236ea and HFC-245eb and that these two products can be simultaneously dehydrofluorinated to produce HFO-1225ye and HFO-1234yf, respectively. Processing conditions are taught to be adjustable, so as to favor the selective conversion of one hydrofluoroolefin over the other. Catalysts that may be used for such reactions were taught to include metal catalysts, 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 $SbCl_5$), aluminum-based catalyst (such as AlF_3, Al_2O_3, and fluorinated Al_2O_3), palladium-based catalysts, platinum-based catalysts, rhodium-based catalysts and ruthenium-based catalysts, including combinations thereof.

[0008] Other examples of methods for the production of HFO-1225ye and HFO-1234yf are set forth in, at least, U.S. Pat. No. 7,560,602, which is assigned to the assignee of the present invention and is incorporated herein by reference. This patent discloses a similar dehydrohalogenation process for producing 2,3,3,3-tetrafluoropropene (1234yf) and 1,1,1,2,3-pentafluoropropene (HFO-1225ye) by catalytic dehydrofluorination of 1,1,1,2,3-pentafluoropropane (245eb) and 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), respectively. Preferred dehydrohalogenation catalysts include fluorinated chromium oxide catalysts, aluminum fluoride catalysts, ferric fluoride catalysts, mixtures of magnesium fluoride and aluminum fluoride catalysts, nickel-based catalysts, carbon based catalysts, and combinations thereof.

[0009] Alternative agents for such dehydrohalogenation reactions are also known. U.S. Patent Application Publication No. 20100029997, for example, teaches the production of hydroolefins (e.g. HFO-1234yf) by dehydrohalogenating HFC-245eb by contacting it to potassium hydroxide (KOH), sodium hydroxide (NaOH), $Ca(OH)_2$, CaO, and combinations thereof. While, in certain embodiments, dehydrohalogenation agents include KOH, alternative agents also include LiOH, $Mg(OH)_2$ and NaOH.

[0010] Applicants have come to appreciate that during continuous processing using such dehydrohalogenation agents (also referred to as "reagent"), the reaction proceeds until either the organic reactants or dehydrohalogenation agent is consumed. Upon completion of the reaction,

the reactor must be dismantled to remove the salt and/or salt solutions. This, in turn creates higher operating costs and reduces productivity. Accordingly, more efficient process is desirable for removal of spent reagent and recycle of unused or regenerated reagent and/or unused organics during a continuous process.

[0011] Applicants assert that the instant invention addresses the foregoing needs.

SUMMARY OF THE INVENTION

[0012] The instant invention relates, at least in part, to a method of increasing the cost efficiency for dehydrohalogenation production of a fluorinated olefin by recovering and recycling spent reagent. In one aspect, the present invention relates to dehydrohalogenating a fluorinated alkane (e.g. pentafluoropropanes and/or hexafluoropropanes) in the presence of a dehydrohalogenating agent to produce a fluorinated olefin (e.g. tetrafluoropropenes and/or pentafluoropropenes). Such dehydrohalogenating agents may include, but are not limited to, potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$), lithium hydroxide (LiOH), magnesium hydroxide ($Mg(OH)_2$), calcium oxide (CaO), or combinations thereof. Removal of spent dehydrohalogenating agent from the reactor allows for facile separation of the organic and the dehydrohalogenating agent. This in turn leads to lower cost associated with design and operation of complicated and highly specialized separation equipment. Recycling the spent dehydrohalogenating agent leads to greater efficiency. Increased productivity is similarly observed if metal fluoride salts are also isolated from the product stream, converted back to the dehydrohalogenating agent's original form, and recycled to the reaction.

[0013] In one aspect, the instant invention relates to a method or process for manufacturing a fluoroolefin including: (a) hydrogenating a first haloolefin to produce a haloalkane; (b) optionally separating said haloalkane into a plurality of intermediate product streams comprising two or more streams selected from the group consisting of a first rich in at least a first alkane, a second stream rich in a second alkane and an alkane recycle stream; (c) dehydrohalogenating the haloalkane in (a) or (b) in the presence of a dehydrohalogenating agent to produce a second haloolefin; (d) withdrawing a reaction stream comprising spent dehydrohalogenating agent and, optionally, metal fluoride salt by products; and (d) recovering, purifying and/or regenerating spent dehydrohalogenating agent. The first haloolefin may include a compound of formula (I)

$$(CX_nY_{3-n})(CR^1_aR^2_b)_zCX=CH_mX_{2-m} \text{ (I)}$$

wherein each X is independently Cl, F, I or Br, provided that at least two Xs are F; each Y is independently H, Cl, F, I or Br; each R^1 is independently H, Cl, F, I, Br or unsubstituted or halogen substituted methyl or ethyl radical; each R_2 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 0, 1 or 2, provided that a+b = 2; m is 0, 1 or 2; and z is 0, 1, 2 or 3.

[0014] In further embodiments of the foregoing, the first haloolefin is comprised of a compound of formula (IA)

$$CX_nY_{3-n}CX=CH_mX_{2-m} \text{ (IA)}$$

wherein each X is independently Cl, F, I or Br, provided that at least two Xs are F; each Y is independently H, Cl, F, I or Br; n is 1, 2 or 3; and m is 0, 1 or 2.

[0015] In even further embodiments of the foregoing, the first haloalkane is hexafluoropropylene (HFP).

[0016] The first haloalkane of the reaction process may be, in certain embodiments, any compound of formula (II)

$$(CX_nY_{3-n})(CR^1_aR^2_b)_ZCHXCH_{m+1}X_{2-m} \text{ (II)}$$

wherein each X is independently Cl, F, I or Br, provided that at least two Xs are F; each Y is independently H, Cl, F, I or Br; each R^1 is independently H, Cl, F, I, Br or unsubstituted or halogen substituted methyl or ethyl radical; each R_2 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 0, 1 or 2, provided that a+b = 2; m is 0, 1 or 2; and z is 0, 1, 2 or 3.

[0017] In further embodiments of the foregoing, the haloalkane is a compound of formula (IIA):

$$(CX_nY_{3-n})CHXCH_{m+1}X_{2-m} \text{ (IIA)}$$

wherein each X is independently Cl, F, I or Br, provided that at least two Xs are F; each Y is independently H, Cl, F, I or Br; n is 1, 2 or 3; and m is 0, 1 or 2.

[0018] In even further embodiments of the foregoing, the intermediate haloalkane is 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and/or 1,1,1,2,3-pentafluoropropane (HFC-245eb).

[0019] The second haloolefin may be, in certain embodiments, any compound of the formula (III):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_ZCX{=}CH_{m+1}X_{1-m} \text{ (III)}$$

wherein each X is independently Cl, F, I or Br, provided that at least two Xs are F; each Y is independently H, Cl, F, I or Br; each R^1 is independently H, Cl, F, I, Br or unsubstituted or halogen substituted methyl or ethyl radical; each R_2 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 0, 1 or 2, provided that a+b = 2; m is 0 or 1; and z is 0, 1, 2 or 3.

[0020] In further embodiments of the foregoing, the second haloolefin is comprised of a compound of the formula (IIIA):

$$(CX_nY_{3-n})CX= CH_{m+1}X_{1-m} \text{ (IIIA)}$$

wherein each X is independently Cl, F, I or Br, provided that at least two Xs are F; each Y is independently H, Cl, F, I or Br; n is 1, 2 or 3; and m is 0 or 1.

[0021] In even further embodiments of the foregoing, the second haloolefin is 2,3,3,3-tetrafluoropropene (1234yf) and/or 1,1,1,2,3-pentafluoropropene (HFO-1225ye).

[0022] In embodiments where the second haloolefin is HFO-1225ye and/or HFO-1234yf, for example, the foregoing reactions can be produced in a single facility having four unit operations. More specifically, hydrogenation of HFP with hydrogen is known to yield both HFC-236ea and HFC-245eb. Like HFC-236ea, HFC-245eb subsequently can be dehydrofluorinated to produce a desirable product. In particular, HFC-236ea can be dehydrofluorinated to produce HFO-1225ye and HFC-245eb can be dehydrofluorinated to produce HFO-1234yf. Thus, both HFO-1225ye and HFO-1234yf can be produced using a single set of four unit operations: hydrogenation of the starting material, separation of the desired intermediate, dehydrofluorination of the intermediate to produce the desired product, followed by another separation to isolate the desired product. For example, in a one system, HFP and H_2 are reacted in a hydrogenation reactor to form an intermediate product stream comprising HFC-236ea and/or HFC-245eb. The relative concentrations of HFC-236ea and HFC-245eb is dependant on reaction conditions in the hydrogenation reactor, such as pressure, temperature, and relative concentration of reactants in the reactor. If the desirable end product is HFO-1225ye, then processing conditions preferably favor the production of HFC-236ea. That is, the hydrogenation reactor is operated to produce an intermediate product stream rich in HFC-236ea

which is subsequently separated from the intermediate process stream and fed into a dehydrofluorination reactor to form a final product stream comprising HFO-1225ye. This HFO-1225ye is then separated from the final product stream and recovered as a purified product. If the desirable end product is HFO-1234yf, then processing conditions preferably favor the production of HFC-245eb. That is, the hydrogenation reactor is operated to produce an intermediate product stream rich in HFC-245eb. This can be accomplished by operating the hydrogenation reactor under conditions favorable to convert the HFP into HFC-236ea and then converting the HFC-236ea into HFC-245eb. The HFC-245eb is then separated from the intermediate product stream and fed into a dehydrofluorination reactor to form a final product stream comprising HFO-1234yf. This HFO-1234yf is then separated from the final product stream and recovered as a purified product.

[0023] In addition, when HFO-1234yf is the desired product, HFO-1225ye can be introduced into the hydrogenation reactor at some point and then converted into HFC-245eb. The source of this HFO-1225ye can be either a separate feed stream and/or a recycle stream (i.e., recycling HFO-1225ye derived from HFC-236ea as noted above). The HFC-245eb is again separated from the intermediate product stream and fed into a dehydrofluorination reactor to form a final product stream comprising HFO-1234yf. This HFO-1234yf is then separated from the final product stream and recovered as a purified product.

[0024] With any of the foregoing, the dehydrofluorination steps (e.g. 245eb → 1234yf or 236ea → 1225ye) occurs in the presence of at least one dehydrohalogenating agent, such as, but not limited to, potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$), lithium hydroxide (LiOH), magnesium hydroxide ($Mg(OH)_2$), calcium oxide (CaO), or combinations thereof. The amount of reagent used, or mole ratio of reagent to organic, will

vary depending on the particular parameters present in each embodiment as discussed above, or otherwise herein. In certain embodiments, the mol ratio of dehydrohalogenating agent to organic feeds (e.g. HFC-245eb and/or HFC-236ea) is from less than 1 to 3, preferably 1-1.5.

[0025] Dehydrohalogenation can be performed in any suitable reaction vessel or reactor. In certain non-limiting embodiments, the reactor includes one or a series of Continuously Stirred Tank Reactors (CSTR), where organic (e.g. HFC-236ea and/or HFC-245eb) and dehydrohalogenating agent are fed continuously into the reactor. From the reaction product stream, a stream of spent dehydrohalogenating agent may be withdrawn and purified on a continuous or intermittent basis.

[0026] In certain embodiments, the stream of spent dehydrohalogenating agent further includes one or more dissolved organics, such as, but not limited to HFC-236ea and/or HFC-245eb. The spent dehydrohalogenating agent may be purified from such organics using one or more known separation methods. Such methods include, but are not limited to, distillation and/or phase separation. The resulting dehydrohalogenating agent can then be, optionally, concentrated and recycled back to the dehydrohalogenation reaction independently, or otherwise with one or more organics, as provided herein.

[0027] In further embodiments, the product stream also includes a salt by-product of the dehydrohalogenation reaction. The salt by-product may be isolated from the product stream using known techniques and converted back to the dehydrohalogenating agent using known methods. It may then be recycled to the dehydrohalogenation reaction independently or with one or more of the organics provided herein. By way of non-limiting example, one such salt by-product may be potassium fluoride (KF), which is formed when potassium hydroxide is used as

the dehydrohalogenation agent. KF may be converted to KOH by treatment with $Ca(OH)_2$ (calcium hydroxide) according to the reaction:

$$2KF + Ca(OH)_2 \rightarrow 2KOH + CaF_2$$

The resulting KOH can be, optionally, concentrated and recycled back to the dehydrohalogenation reaction independently, or otherwise with one or more organics, as provided herein.

[0028] Additional embodiments and advantages of the instant invention will be readily apparent to one of skill in the art based on the disclosure provided herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] FIG. 1 is a process flow diagram showing the production of fluoroolefins according to an embodiment of the invention.

[0030] FIG. 2 is a process flow diagram showing the hydrogenation unit operation according to an embodiment of the invention.

[0031] FIG. 3 is a process flow diagram showing the hydrogenation unit operation according to another embodiment of the invention.

[0032] FIG. 4 is a process flow diagram showing the first separation unit operation according to an embodiment of the invention.

[0033] FIG. 5 is a process flow diagram showing the first separation unit operation according to another embodiment of the invention.

[0034] FIG. 6 is a process flow diagram showing the dehydrofluorination unit operation according to an embodiment of the invention.

[0035] FIG. 7 is a process flow diagram showing the dehydrofluorination unit operation according to another embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0036] The instant invention relates, at least in part, to a method increasing the cost efficiency for dehydrohalogenation production of a fluorinated olefin by recovering and recycling spent dehydrohalogenation agent. In one aspect, the present invention relates to dehydrohalogenating a fluorinated alkane (e.g. pentafluoropropane and/or hexafluoropropane) in the presence of a dehydrohalogenating agent to produce a fluorinated olefin (e.g. tetrafluoropropenes and/or pentafluoropropenes). Removal of spent dehydrohalogenating agent from the reactor reduces design and operation costs and recycling the spent and/or regenerated dehydrohalogenating agent leads to improved efficiency. In certain embodiments, the dehydrohalogenating agent may include, but is not limited to, potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$), lithium hydroxide (LiOH), magnesium hydroxide (MgOH), calcium oxide (CaO) or combinations thereof. In further embodiments, the dehydrohalogenating agent is potassium hydroxide (KOH).

[0037] In certain embodiments, the fluorinated olefins of the present invention include one or more C3 to C6 fluoroalkenes, preferably compounds having a formula as follows:

$$X^1CF_zR_{3-z}$$

where X^1 is a 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 pentafluoropropenes (HFO-1225) are especially preferred.

[0038] In one embodiment, the processes for producing the fluorinated olefins of the present invention include 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. The fluorinated olefin starting material preferably, though not exclusively, has a degree of fluorine substitution of N+1 and 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 final olefin. This olefin conversion step includes a reaction that is sometimes referred to herein for convenience, but not necessarily by way of limitation, as a reduction or hydrogenation step. The resulting fluorinated alkane is then converted to a fluorinated olefin having a degree of fluorine substitution of N. 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 particularly in certain embodiments as a dehydrofluorination or dehydrochlorination reaction.

[0039] Based on the foregoing, in one aspect of the present invention, the processes for producing a fluoroolefin includes the following steps:

(a) hydrogenating a compound of formula (I):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_zCX{=}CH_mX_{2-m} \quad (I)$$

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

$$(CX_nY_{3-n})(CR^1_aR^2_b)_zCHXCH_{m+1}X_{2-m} \quad (II)$$

where:

each X is independently Cl, F, I or Br, provided that at least two Xs are F;

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

each R^1 is independently H, Cl, F, I, Br or unsubstituted or halogen substituted methyl or ethyl radical;

each R_2 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 0, 1 or 2, provided that a+b = 2;

m is 0, 1 or 2; and

z is 0, 1, 2 or 3; and

(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):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_ZCX=CH_{m+1}X_{1-m} \text{ (III)}$$

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

[0040] In further non-limiting embodiments, the reactant of formula (I) may include a three carbon olefin of formula (IA) wherein z is 0, namely

$$CX_nY_{3-n}CX=CH_mX_{2-m} \text{ (IA)}$$

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

$$(CX_nY_{3-n})CHXCH_{m+1}X_{2-m} \text{ (IIA)}$$

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

$$(CX_nY_{3-n})CX= CH_{m+1}X_{1-m} \text{ (IIIA)}$$

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

[0041] In even further embodiments, the instant invention provides a saturated terminal carbon of the compounds of formulas (I) or (IA) that is fully substituted with fluorine (for example, n on the saturated terminal carbon is 3 and each X on that carbon is F). In such embodiments, the compound of Formula (I) or (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 is 3, m is 1, and all X are F). the resulting compound of formula (II) or (IIA) is selected from the group consisting of, one or more of the following fluorinated alkanes: 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.

[0042] In any of the foregoing reactions, 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) or (IA) to produce a compound of formula (II) is conducted under conditions effective to provide a formula (II) or (IIA) 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%.

[0043] In any of the foregoing reactions, 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%.

THE HYDROGENATION STEP

[0044] 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. While it is contemplated that the hydrogenation reaction may be conducted in a single reaction vessel, this reaction step 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.

[0045] While it is possible that the reaction may involve in certain embodiments a liquid phase reaction, it is contemplated that in certain embodiments the hydrogenation reaction comprises at least one vapor phase reaction stage.

[0046] In one embodiment of the present invention, as illustrated in Figure 2, 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. 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 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 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 or reducing agent, preferably H_2, 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 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/or separated, the content of recycle stream 4, when present, preferably being relatively rich in HFC-236ea, HFC-245eb, or a combination of these.

[0047] In another preferred embodiment of the present invention as illustrated in Figure 3, the hydrogenation step comprises at least a first reaction step A1 and a second reaction step A2. In one embodiment, 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. 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 2A comprises the hydrogenation agent, preferably H_2, 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 been cooled and/or separated, the content of recycle stream 4, when present, preferably being relatively rich in HFC-236ea, HFC-245eb, or a combination of these.

[0048] In connection with the reaction stage converting HFP in the hydrogenation reactor at step A1, it is preferred in certain embodiments to use a trickle bed reactor. It is contemplated that the reaction is such case proceeds as follows:

$$CF_3CF=CF_2 + H_2 \rightarrow CF_3CHFCF_2H \text{ (HFC-236ea).}$$

A major side reaction of this process yields HFC-245eb and HF. It is believed that 245eb is formed from 236ea by hydrodefluorination and/or by dehydrofluorination followed by reduction:

$$\text{HFC-236ea} + H_2 \rightarrow \text{HFC-245eb} + \text{HF.}$$

[0049] The second reaction step A2, 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 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 1B, when present, comprises HFO-1225ye, and preferably substantially all of the HFO-1225ye being fed to the reaction step A. The second path or feed stream 2B comprises the hydrogenation agent, preferably H_2, 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.

[0050] In connection with the reaction stage converting HFO-1225ye in the hydrogenation reactor at step A2, it is preferred in certain embodiments to use a trickle bed reactor. It is contemplated that the reaction is such case proceeds as follows:

$$CF_3CF=CFH\ (liq) + H_2\ (gas) \rightarrow CF_3CHFCFH_2\ (HFC\text{-}245eb\ -\ gas)$$

A major side reaction is contemplated to be:

$$HFC\text{-}245eb + H_2 \rightarrow CF_3CHFCH_3\ (HFC\text{-}254) + HF$$

[0051] 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, 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.

[0052] 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 carbon, either alone or in combination with other catalysts. In this regard one or more of the hydrogenation catalysts disclosed in US Patent 5, 679,875, which is incorporated herein by reference, may be 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.

[0053] Thus, certain embodiments of the present methods comprise bringing a fluorinated olefin in accordance with formula I and a hydrogenation agent, such as H_2, 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 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 about from 75°C to about 115°C, and even more preferably from about 90°C to about 100°C.

[0054] 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 100 psig to about 300 psig, preferably about from 150 psig to about 250 psig, and even more preferably about 200 psig.

[0055] Applicants have found, without being bound by or to any particular theory, that the use of a cooled recycle stream 4, 4A, or 4B 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.

[0056] 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 H_2: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

[0057] In certain preferred embodiments, the present invention also includes the step of cooling at least a portion reactor product stream (3, 3A, 3B) 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 50 ºC to about 100 ºC, and even more preferably about 70 ºC. 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.

[0058] 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 and/or HFC-245eb, is also produced from the separation step B2.

[0059] 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.

[0060] 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-245eb 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 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

[0061] The dehydrofluorination step can be carried out in a liquid phase in the presence of a dehydrohalogenation agent (e.g. caustic solution) or a gas phase in the presence of a dehydrofluorination catalyst. It is contemplated that the reaction may be carried out batchwise, continuously or a combination thereof.

[0062] In one embodiment the converting step involves a reaction in which HFC-245eb and/or HFC-236ea is contacted with a dehydrohalogenating agent such as KOH, NaOH, $Ca(OH)_2$, LiOH, $Mg(OH)_2$, CaO, and combinations thereof to form the fluorinated olefin. By way of example, if KOH is used, such a reaction may be described by way of illustration, but not necessarily by way of limitation, by the following reaction equations (1) and (2):

$$CF_3\text{-}CHF\text{-}CHF_2 + KOH \rightarrow CF_3CF{=}CHF + KF + H_2O \quad (1)$$

$$CF_3\text{-}CHF\text{-}CH_2F + KOH \rightarrow CF_3CF{=}CH_2 + KF + H_2O \quad (2)$$

[0063] The dehydrohalogenating agent may be provided as a caustic aqueous solution comprising from about 2% to about 100%, more preferably from about 10% to about 50%, and even more preferably from about 10% to about 30% by weight of dehydrohalogenating agent. In further embodiments, the caustic solution, and preferably the dehydrohalogenating agent solution, is brought to a temperature of from about 20°C to about 100°C, more preferably from about 20°C to about 90°C, and most preferably from about 20°C to about 70°C. The reaction pressure in such embodiments may vary, depending on particular processing parameters of each application. In certain embodiments, the reaction pressure ranges from atmospheric pressure, super-atmospheric pressure or under vacuum. The vacuum pressure, when used, in certain embodiments ranges from about 5 torr to about 760 torr.

[0064] It is contemplated that the amount of dehydrohalogenation agent (or reagent) used, or mole ratio of reagent to organic, will vary depending on the particular parameters present in each embodiment. In certain embodiments, the mol ratio of dehydrohalogenating agent to organic feeds (e.g. HFC-245eb and/or HFC-236ea) is from less than 1 to 3, preferably 1-1.5. In further embodiments, the contact time, which is expressed as the ratio of the volume of the reagent (ml) to the total feed flow (ml/sec) is from about 0.1 seconds to about 1000 seconds, and preferably from about 2 seconds to about 120 seconds.

[0065] The dehydrohalogenation reactions can be accomplished using any suitable vessel or reactor. Such vessels or reactors should be constructed from materials which are resistant to corrosion, such as stainless steel, nickel and its alloys, including Hastelloy, Inconel, Incoloy, and Monel. In certain embodiments, this reaction is performed using one or a series of Continuously Stirred Tank Reactors (CSTR). In this type of reactor, organic feed (e.g. HFC-236ea and/or HFC-245eb) and dehydrohalogenating agent would be fed continuously into the reactor and the resulting product stream formed would be fed into a condenser or distillation column for separation of 1225ye and/or 1234yf from and un-reacted 236ea and/or 245eb, as well as other by-products of the reaction.

[0066] In certain embodiments, spent dehydrohalogenating agent is removed from the product stream either periodically or continuously and is recycled back to the reactor for reuse. As noted previously, Applicants have discovered that, during continuous processing the reaction proceeds until either the organic reactants (e.g. HFC-236ea and/or HFC-245eb) or dehydrohalogenating agent is consumed. This increases costs of productivity because the reactor must be dismantled upon completion of the reaction to remove the salt and/or salt solutions. By

recycling the dehydrohalogenating agent and by-product salts, however, such costs may be reduced and the system made more efficient.

[0067] Spent dehydrohalogenating agent and by-product salts (e.g. metal fluoride salts) may be withdrawn from the reactor by a product stream either continuously or intermittently using one or more known separation techniques. To this end, spent dehydrohalogenating agent separation may occur using any known compound separation techniques, such, but not limited to, distillation, phase separation, etc. In certain embodiments, withdrawal of spent dehydrohalogenating agent is especially beneficial for component separation as it allows for facile separation of organic and dehydrohalogenating agent. This in turn leads to lower cost associated with design and operation of complicated and highly specialized separation equipment.

[0068] The product stream containing spent dehydrohalogenating agent typically carries with it some dissolved organic (e.g. HFC-236ea and/or HFC-245eb). By stopping the stirrer and then removing spent dehydrohalogenating agent during the time agitation is stopped, separation of dehydrohalogenating agent and such organic can be facilitated. Spent dehydrohalogenating agent and dissolved organic would be taken into a container where additional separation of dehydrohalogenating agent and organic can be accomplished using one or more of the foregoing separation techniques. In one non-limiting embodiment, for example, KOH is separation by distillation, i.e. by heating organic just above boiling point of 236ea and/or 245eb, thus fractionating the organic from the spent KOH. Alternatively, one can use phase separator to separate between the two phases. The organic free KOH isolate can be immediately recycled to the reactor or can be concentrated and the concentrated solution can be returned to reactor.

[0069] The by-product salt can also be isolated and converted back to the dehydrohalogenating agent used known methods. When KOH is used as the dehydrohalogenating agent, for example, KF is formed as a by-product salt. Such salt may be converted back to KOH and recycled back to the dehydrohalogenation reaction. For example, $Ca(OH)_2$ can be used for KF conversion according to reaction below.

$$2KF + Ca(OH)_2 \rightarrow 2KOH + CaF_2$$

CaF_2 will precipitate from the foregoing reaction while KOH is isolated and recycled back to reactor. Recycling of spent dehydrohalogenating agent leads to better efficiency of the reagent use. Moreover, the use of recycling of the by-product salt reduces dehydrohalogenating agent use, reduces costs of reagents and costs associated with disposal of the salt, and/or purchase of new raw material.

[0070] In one embodiment of the present invention, and referring to Figure 6, 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. 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-245eb, and preferably substantially all of the HFO-245eb 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/or

separated. The content of recycle stream 8, when present, may include unreacted organic (e.g. HFC-236ea, HFC-245eb) and spent dehydrohalogenating agent. Each may be purified or recovered, as provided herein and recycled.

[0071] 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 C2, 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 8B, 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 or recycled dehydrohalogenating agent, as defined herein. 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.

[0072] 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 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, 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.

[0073] The resulting products may be isolated from the product stream using one or more methods known in the art and purified accordingly.

EXAMPLES

[0074] The following examples are provided for the purpose of illustrating the present invention but without limiting the scope thereof.

[0075] Example 1:

[0076] A CSTR (Continuously Stirred Tank Reactor) was used to convert 245eb to 1234yf. The reactor was designed and operated in such a way that the end of the dip tube was in the middle of KOH phase. After the startup, organic and fresh KOH were constantly fed in. Organic out (the overhead portion) was constantly taken out. In a typical cycle organic and KOH flow in and overhead is taken out for 30 min. Flowrates were 5 and 12 ml/min, respectively. The mixture is stirred during this period of time. Then stirrer is stopped for 10 min, while feeds still go in. While stirrer is off, after 10 min, applicable valves for the spent KOH to go out were open. Between 500 and 550 g was taken out every 40 min.

[0077] Experiment was carried out for 7 hours. Temperature was 48 °C. Pressure was 45 psig. GC area percent of the organic feed was ~97% of 245eb, the rest being most probably 254. The flowrates translate to mol ratio of KOH to G-245eb of 1, or slightly above 1. Theoretical residence time was 100 min.

[0078] Scrubber Product Collection Cylinder (SPCC) was used to collect spent KOH and the portion of organic that was carried out with spent KOH. Organic was trapped in methylene chloride which was previously added to SPCC. The volume of methylene chloride inside the SPCC was 15% of the total volume of liquid in SPCC. Product and un-reacted organic was collected in a Product Collection Cylinder (PCC) that was held in dry ice. Vapor samples were taken once per hour while liquid samples were taken at much longer intervals.

[0079] Overall mass balance was 94% for organic. Average conversion was 48%. Selectivity to 1234yf was 73%.

[0080] Example 2:

[0081] The second experiment was carried out in the same fashion as the experiment 1, except that pressure and temperature were 48 psig and 47 °C. Experiment lasted 6 hours and overall conversion was 69%. Selectivity to 1234yf was 75%.

[0082] Example 3:

[0083] Reactor was loaded with 807 ml of organic. The feed was analyzed by GC to reveal Area % for 236ea as 97.70%. There was no 1234yf in this feed, while the percentage of 1225ye was 0.03. After loading the reactor with organic, 1641 ml of 25% KOH was added. Therefore mol ratio of KOH to 236ea was 1.23.

[0084] The flowrates of 236ea and KOH were 2 and 4 ml/min. Pressure was 35-45 psig. Reactor temperature was 42-45 °C.

[0085] Spent KOH was taken out of reactor periodically (it was fed continuously as was organic; overhead product was taken out continuously, i.e. semi-continuous operation). In this semi-continuous mode KOH and organics flowed into stirred reactor for 50 min. Then the stirrer was stopped for 10 min while reactants were still going in. Afterwards 290-300 g of spent KOH was taken out. Then stirrer was started as was the clock for 50 min time period.

[0086] Spent KOH was collected in Scrubber Product Collection Cylinder (SPCC). SPCC was pre-filled with methylene chloride (the target was to have 15-20 wt% of methylene chloride in the final spent KOH- methylene chloride solution). Analysis of methylene chloride layer revealed that ~70 GC area % was 236ea. There was small amount of 1225ye (~2%) while the rest were unidentified heavies. In order to confirm that all organic was extracted with

methylene chloride , part KOH was added to part $MeCl_2$ (i.e. 1:1). GC analysis revealed that amount of organic was negligible.

[0087] Overall mass balance was 88.67%. Residence time was 200 min. The conversion was ~50%. Selectivity to 1225ye was 63%. The reaction was carried out for the total of 97 hours.

CLAIMS

What is claimed is:

1. A method for producing at least one fluorinated olefin comprising:

a. hydrogenating a starting material stream comprising at least one alkene according to Formula (I):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_zCX=CH_mX_{2-m} \qquad (I)$$

by contacting said starting material with a reducing agent to produce an intermediate product stream comprising at least one alkane according to Formula (II):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_zCHXCH_{m+1}X_{2-m} \qquad (II)$$

where:

each X is independently Cl, F, I or Br, provided that at least two Xs are F;

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

each R^1 is independently H, Cl, F, I, Br or unsubstituted or halogen substituted methyl or ethyl radical;

each R_2 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 0, 1 or 2, provided that a+b = 2;

m is 0, 1 or 2; and

z is 0, 1, 2 or 3;

b. optionally, separating said intermediate product stream into a plurality of intermediate product streams, said plurality of intermediate product streams comprising two or more streams selected from the group consisting of a first

stream rich in at least a first alkane according to Formula II, a seconds stream rich in at least a second alkane according to Formula II, and an alkane recycle stream;

c. dehydrofluorinating, in the presence of a dehydrohalogenating agent, at least a portion of said intermediate process stream from step (a) or said plurality of intermediate process streams of step (b) to produce an alkene product stream comprising 1,1,1,2,3-pentafluoropropene and at least one additional alkene having a lower degree of fluorine substitution compared to the degree of fluorination of the compound of formula (I); and

d. withdrawing from a dehydrofluorinated product stream a product reaction stream comprising spent dehydrohalogenating agent; and

e. recovering spent dehydrohalogenating agent.

2. The method of claim 1 wherein said additional alkene is a compound according to formula (III):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_ZCX{=}CH_{m+1}X_{1-m} \text{ (III)}$$

where each of X, Y, R^1, R^2, n, a, and b is the same value as in formula (I) and m is 0 or 1.

3. The method of claim 2 wherein Z is 0.

4. The method of claim 3 wherein m is 0 or 1.

5. The method of claim 4 wherein said n is 3.

6. The method of claim 5 wherein X is F.

7. The method of claim 1 wherein said reducing agent is H_2.

8. The method of claim 1 wherein said starting material stream comprises hexafluoropropylene and said additional alkene is 1,1,1,2-tetrafluoropropene.

9. The method of claim 1 wherein the dehydrohalogenating agent is selected from the group consisting of KOH, NaOH, $Ca(OH)_2$, LiOH, $Mg(OH)_2$, CaO, and combinations thereof.

10. A method for producing 1,1,1,2-tetrafluoropropene comprising:

a. hydrogenating a starting material stream comprising hexafluoropropylene by contacting said starting material stream with a reducing agent in a hydrogenation reactor to produce an intermediate stream comprising 1,1,1,2,3-pentafluoropropane or 1,1,1,2,3,3-hexafluoropropane;

b. dehydrofluorinating, in the presence of a dehydrohalogenating agent, said 1,1,1,2,3-pentafluoropropane or said 1,1,1,2,3,3-hexafluoropropane in a dehydrofluorination reactor to produce a product stream comprising 1,1,1,2-tetrafluoropropene or 1,1,1,2,3-pentafluoropropene;

c. withdrawing from the product stream a second product stream comprising spent dehydrohalogenating agent; and

d. recovering spent dehydrohalogenating agent.

11. The process of claim 10 wherein the second product stream further comprises one or more dissolved organics.

12. The process of claim 11 wherein the dissolved organics are selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,2,3-pentafluoropropane (HFC-245eb), and combinations thereof.

13. The process of claim 10 wherein the spent dehydrohalogenating agent is purified using at least one separation method.

14. The process of claim 13 wherein the separation method is selected from the group consisting of distillation or phase separation.

15. The process of claim 10 further comprising, optionally, concentrating the purified dehydrohalogenating agent and recycling it back to the dehydrohalogenation reaction.

16. The process of claim 10 wherein the reaction stream further comprises by-product salts of the dehydrohalogenating agent.

17. The process of claim 16 further comprising converting the by-product salts to the dehydrohalogenating agent.

18. The process of claim 16 wherein the dehydrohalogenating agent is KOH and the by-product salt is KF.

19. The process of claim 18 further comprising, optionally, concentrating the converted KOH and recycling it back to the dehydrohalogenation reaction.

20. The process of claim 18 further comprising converting KF to KOH in the presence of $Ca(OH)_2$.

21. A process for the manufacture of a fluoroolefin comprising:

(a) dehydrohalogenating a haloalkane in the presence of KOH to produce a haloalkene;

(b) withdrawing a reaction stream comprising spent KOH; and

(c) recovering spent KOH.

22. The process of claim 21 wherein the haloalkane is comprised of a compound of formula (IIA):

$$(CX_nY_{3-n})CHXCH_{m+1}X_{2-m} \quad (IIA)$$

wherein each X is independently selected from the group consisting of Cl, F, I and Br; each Y is independently selected from the group consisting of H, Cl, F, I, and Br; n is 1,2, or 3; and m is 0, 1 or 2.

23. The process of claim 22 wherein the haloalkane is 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb).

24. The process of claim 21 wherein the haloalkene is comprised of a compound of formula (IIIA):

$$(CX_nY_{3-n})CX=CH_{m+1}X_{1-m} \quad \text{(IIIA)}$$

wherein each X is independently selected from the group consisting of Cl, F, I and Br; each Y is independently selected from the group consisting of H, Cl, F, I, and Br; n is 1,2, or 3; and m is 0 or 1.

25. The process of claim 24 wherein the haloalkene is 2,3,3,3-tetrafluoropropane (HFO-1234yf) or 1,2,3,3,3-pentafluoropropene (HFO-1225ye).

26. The process of claim 21 wherein the dehydrohalogenation occurs using a continuously stirred tank reactor.

27. The process of claim 21 wherein the spent KOH is withdrawn from the reactor continuously or intermittently.

28. The process of claim 21 wherein the reaction stream further comprises a dissolved organics.

29. The process of claim 28 wherein the dissolved organics are selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb).

30. The process of claim 21 wherein the spent KOH is purified using at least one separation method.

31. The process of claim 30 wherein the separation method is selected from the group consisting of distillation or phase separation.

32. The process of claim 21 further comprising, optionally, concentrating the purified KOH and recycling it back to the dehydrohalogenation reaction.

33. The process of claim 21 wherein the reaction stream further comprises KF.

34. The process of claim 3 further comprising converting KF to KOH in the presence of $Ca(OH)_2$.

35. The process of claim 34 further comprising, optionally, concentrating the converted KOH and recycling it back to the dehydrohalogenation reaction.

36. A process for the manufacture of a fluoroolefin comprising:

(a) dehydrohalogenating 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb) in the presence of KOH to produce 2,3,3,3-tetrafluoropropane (HFO-1234yf) or 1,2,3,3,3-pentafluoropropene (HFO-1225ye);

(b) withdrawing a reaction stream comprising spent KOH; and

(c) recovering spent KOH.

37. The process of claim 36 wherein the dehydrohalogenation occurs using a continuously stirred tank reactor.

38. The process of claim 36 wherein the spent KOH is withdrawn from the reactor continuously or intermittently.

39. The process of claim 36 wherein the reaction stream further comprises a dissolved organics.

40. The process of claim 37 wherein the dissolved organics are selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb).

41. The process of claim 36 wherein the spent KOH is purified using at least one separation method.

42. The process of claim 41 wherein the separation method is selected from the group consisting of distillation or phase separation.

43. The process of claim 36 further comprising, optionally, concentrating the purified KOH and recycling it back to the dehydrohalogenation reaction.

44. The process of claim 36 wherein the reaction stream further comprises KF.

45. The process of claim 44 further comprising purifying KF from the reaction stream.

46. The process of claim 36 further comprising converting KF to KOH in the presence of $Ca(OH)_2$, optionally, concentrating the KOH and recycling it back to the dehydrohalogenation reaction.

ABSTRACT

The instant invention relates, at least in part, to a method increasing the cost efficiency for dehydrohalogenation production of a fluorinated olefin by recovering and recycling spent dehydrohalogenation agent. In one aspect, the present invention relates to dehydrohalogenating a fluorinated alkane (e.g. pentafluoropropane and/or hexafluoropropane) in the presence of a dehydrohalogenating agent to produce a fluorinated olefin (e.g. tetrafluoropropenes and/or pentafluoropropenes). Removal of spent dehydrohalogenating agent from the reactor allows for facile separation of organic and dehydrohalogenating agent, the latter of which is recycled.

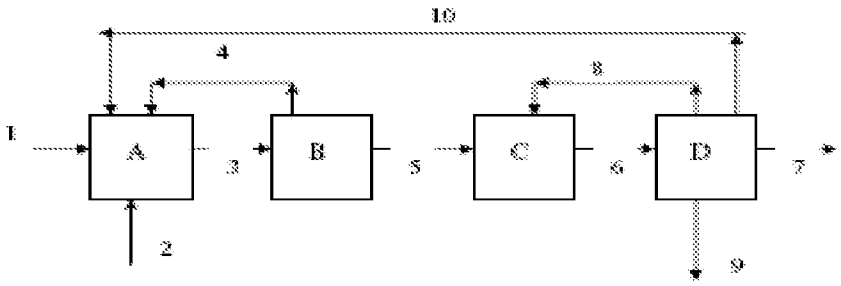

FIGURE 1

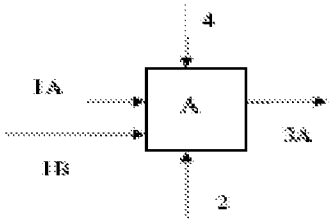

FIGURE 2

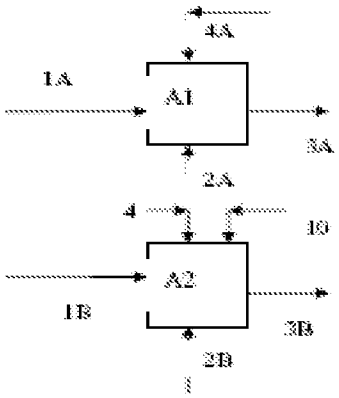

FIGURE 3

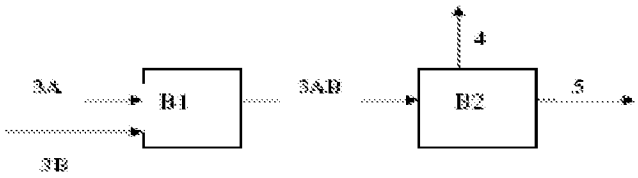

FIGURE 4

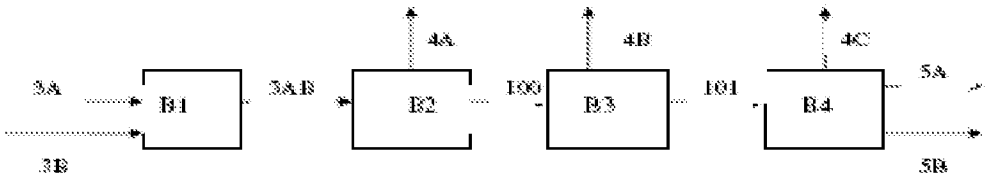

FIGURE 4A

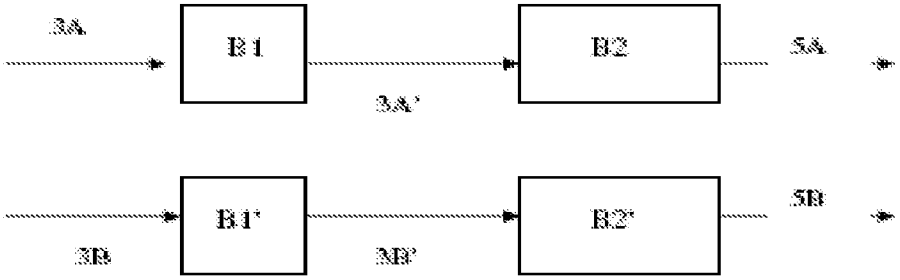

FIGURE 5

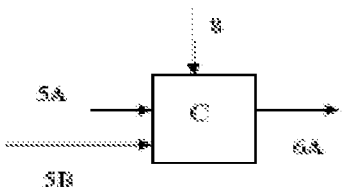

FIGURE 6

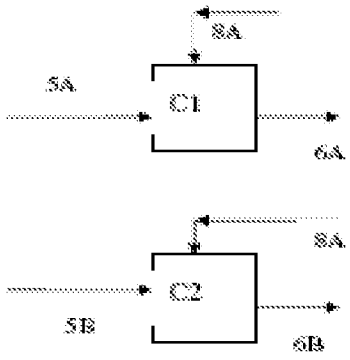

FIGURE 7

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS
First Named Inventor/Applicant Name:	SELMA BEKTESEVIC
Filer:	John Eric Sumner/Michele Greenberg
Attorney Docket Number:	H0024680-4511

Filed as Large Entity

Utility under 35 USC 111(a) Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Utility application filing	1011	1	330	330
Utility Search Fee	1111	1	540	540
Utility Examination Fee	1311	1	220	220
Pages:				
Claims:				
Claims in excess of 20	1202	26	52	1352
Independent claims in excess of 3	1201	1	220	220
Miscellaneous-Filing:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**2662**

Electronic Acknowledgement Receipt

EFS ID:	10915741
Application Number:	13229016
International Application Number:	
Confirmation Number:	8706
Title of Invention:	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS
First Named Inventor/Applicant Name:	SELMA BEKTESEVIC
Customer Number:	91970
Filer:	John Eric Sumner/Michele Greenberg
Filer Authorized By:	John Eric Sumner
Attorney Docket Number:	H0024680-4511
Receipt Date:	09-SEP-2011
Filing Date:	
Time Stamp:	15:40:17
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$2662
RAM confirmation Number	2409
Deposit Account	
Authorized User	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)

1	Application Data Sheet	intCB.PDF	1105248 ac70a7ca70a3679483b49256a04ab90855d2b1ea	no	5
Warnings:					
Information:					
2		intCC.PDF	169302 7b969af47a9c18d40144701d6f282a2cb39456f9	yes	39

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Specification	1	31
	Claims	32	38
	Abstract	39	39

Warnings:					
Information:					
3	Drawings-only black and white line drawings	intCD.PDF	33777 2924ced1b8bc7049246af5510df9b229ba302f0d	no	3
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Information:					
4	Fee Worksheet (SB06)	fee-info.pdf	38056 3262caf096aad6ae51cae0c3623f17daa08ecebf	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	1346383		

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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.

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
13/229,016	09/09/2011	SELMA BEKTESEVIC	H0024680-4511

CONFIRMATION NO. 8706

91970
HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962

FORMALITIES LETTER

OC00000049947379

Date Mailed: 09/23/2011

NOTICE TO FILE MISSING PARTS OF NONPROVISIONAL APPLICATION

FILED UNDER 37 CFR 1.53(b)

Filing Date Granted

Items Required To Avoid Abandonment:

An application number and filing date have been accorded to this application. The item(s) indicated below, however, are missing. Applicant is given **TWO MONTHS** from the date of this Notice within which to file all required items below to avoid abandonment. Extensions of time may be obtained by filing a petition accompanied by the extension fee under the provisions of 37 CFR 1.136(a).

- The oath or declaration is missing.
  A properly signed oath or declaration in compliance with 37 CFR 1.63, identifying the application by the above Application Number and Filing Date, is required.
  Note: If a petition under 37 CFR 1.47 is being filed, an oath or declaration in compliance with 37 CFR 1.63 signed by all available joint inventors, or if no inventor is available by a party with sufficient proprietary interest, is required.

The applicant needs to satisfy supplemental fees problems indicated below.

The required item(s) identified below must be timely submitted to avoid abandonment:

- A surcharge (for late submission of filing fee, search fee, examination fee or oath or declaration) as set forth in 37 CFR 1.16(f) of $**130** for a non-small entity, must be submitted.

SUMMARY OF FEES DUE:

Total fee(s) required within **TWO MONTHS** from the date of this Notice is $**130** for a non-small entity
- $**130** Surcharge.

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PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 13/229,016

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	330
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	540
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	220
TOTAL CLAIMS (37 CFR 1.16(i))	46 minus 20 =	* 26			OR	x 52 =	1352
INDEPENDENT CLAIMS (37 CFR 1.16(h))	4 minus 3 =	* 1				x 220 =	220
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $270 ($135 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	2662

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
13/229,016	09/09/2011	1621	2662	H0024680-4511	46	4

CONFIRMATION NO. 8706

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HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962

FILING RECEIPT

OC00000049947378

Date Mailed: 09/23/2011

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Applicant(s)

SELMA BEKTESEVIC, Williamsville, NY;
HSUEH SUNG TUNG, Getzville, NY;
HALUK KOPKALLI, Staten Island, NY;

Assignment For Published Patent Application

HONEYWELL INTERNATIONAL INC., Morristown, NJ

Power of Attorney: None

Domestic Priority data as claimed by applicant

This appln claims benefit of 61/392,242 10/12/2010
and is a CIP of 13/195,429 08/01/2011
which is a CIP of 12/402,372 03/11/2009 PAT 8,013,194
which claims benefit of 61/036,526 03/14/2008

Foreign Applications (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.)

If Required, Foreign Filing License Granted: 09/20/2011

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 13/229,016**

Projected Publication Date: To Be Determined - pending completion of Missing Parts

Non-Publication Request: No

Early Publication Request: No

Title

INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS

Preliminary Class

570

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

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For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4158).

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Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

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The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor:	**SELMA BEKTESEVIC, ET AL.**	Examiner:	**Not Yet Assigned**
Application No.:	**13/229,016** Conf. No. **8706**	Group Art Unit:	**1621**
Filed:	**September 9, 2011**	Docket No.:	**H0024680-4511**

Title: **INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS**

FILED ELECTRONICALLY

Mail Stop: Missing Parts
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

RESPONSE TO NOTICE TO FILE MISSING PARTS DATED SEPTEMBER 23, 2011

Sir:

This is in response to a Notice of Missing Parts mailed September 23, 2011, having a two-month statutory period for response ending October 11, 2011. Applicants submit herewith an executed Inventor's Declaration with the required $130 declaration surcharge.

Applicants believe that no additional fees are due at this time, however, the Office is authorized to charge Applicants' Deposit Account No. 50-1943 for any additional fees that are required to process the application.

Respectfully submitted

Date: October 6, 2011

/J. Eric Sumner/

J. Eric Sumner
Reg. No. 58,699
2000 Market Street, 20th Floor
Philadelphia, PA 19103
Tel: 215-299-2772
Fax: 215-299-2150
Email: esumner@foxrothschild.com

DECLARATION FOR PATENT APPLICATION

For use with Application Data Sheet (*See PTO/SB/01A*)

Title of Invention: INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS

As the below named inventor(s), I/we declare that:

This declaration is directed to:
____ the attached application, or
__X__ **Application No. 113/229,016 filed on September 9, 2011**
___ as amended on _____(if applicable);

I/we believe that I/we am/are the original and first inventor(s) of the subject matter which is claimed and for which a patent is sought;

I/we have reviewed and understand the contents of the above-identified application, including the claims, as amended by any amendment specifically referred to above;

I/we acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me/us to be material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT International filing date of the continuation-in-part application.

Please direct all correspondence: to the address associated with Customer Number **91970.**

Please direct telephone calls: primarily to J. Eric Sumner (Outside Counsel) at 215-299-2772 and secondarily to Bruce Bradford (Honeywell) at 973-455-2362.

All statements made herein of my/our own knowledge are true, all statements made herein on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001, and may jeopardize the validity of the application or any patent issuing thereon.

Signature of Sole or First Inventor: Bektesevic Selma Date: 09/30/2011
Full Name of Sole or First Inventor: **SELMA BEKTESEVIC**
Business Mailing Address: Honeywell International Inc., Patent Services M\S AB\2B, P.O. Box 2245
Morristown, NJ, 07962-2245

Signature of Second Joint Inventor: Hsueh Sung Tung Date: 9/30/2011
Full Name of Second Joint Inventor: **HSUEH SUNG TUNG**
Business Mailing Address: Honeywell International Inc., Patent Services M\S AB\2B, P.O. Box 2245
Morristown, NJ, 07962-2245

Signature of Third Joint Inventor: _____ Date: _____
Full Name of Third Joint Inventor: **HALUK KOPKALLI**
Business Mailing Address: Honeywell International Inc., Patent Services M\S AB\2B, P.O. Box 2245
Morristown, NJ, 07962-2245

DECLARATION FOR PATENT APPLICATION

For use with Application Data Sheet (*See PTO/SB/01A*)

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This declaration is directed to:
___ the attached application, or
__X__ **Application No. 113/229,016 filed on September 9, 2011**
___ as amended on _____(if applicable);

I/we believe that I/we am/are the original and first inventor(s) of the subject matter which is claimed and for which a patent is sought;

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Signature of Sole or First Inventor: _____ Date: _____

Full Name of Sole or First Inventor: SELMA BEKTESEVIC

Business Mailing Address: Honeywell International Inc., Patent Services M\S AB\2B, P.O. Box 2245
Morristown, NJ, 07962-2245

Signature of Second Joint Inventor: _____ Date: _____

Full Name of Second Joint Inventor: HSUEH SUNG TUNG

Business Mailing Address: Honeywell International Inc., Patent Services M\S AB\2B, P.O. Box 2245
Morristown, NJ, 07962-2245

Signature of Third Joint Inventor: Haluk Kopkalli Date: 12-SEP-2011

Full Name of Third Joint Inventor: HALUK KOPKALLI

Business Mailing Address: Honeywell International Inc., Patent Services M\S AB\2B, P.O. Box 2245
Morristown, NJ, 07962-2245

(Rev.11/24/2010)

PH1 2919308v1 09/09/11

Electronic Patent Application Fee Transmittal

Application Number:	13229016
Filing Date:	09-Sep-2011
Title of Invention:	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS
First Named Inventor/Applicant Name:	SELMA BEKTESEVIC
Filer:	John Eric Sumner/Michele Greenberg
Attorney Docket Number:	H0024680-4511

Filed as Large Entity

Utility under 35 USC 111(a) Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Late filing fee for oath or declaration	1051	1	130	130
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
			Total in USD ($)	**130**

Electronic Acknowledgement Receipt

EFS ID:	11127823
Application Number:	13229016
International Application Number:	
Confirmation Number:	8706
Title of Invention:	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS
First Named Inventor/Applicant Name:	SELMA BEKTESEVIC
Customer Number:	91970
Filer:	John Eric Sumner/Michele Greenberg
Filer Authorized By:	John Eric Sumner
Attorney Docket Number:	H0024680-4511
Receipt Date:	06-OCT-2011
Filing Date:	09-SEP-2011
Time Stamp:	16:41:35
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$130
RAM confirmation Number	3232
Deposit Account	
Authorized User	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)

1	Applicant Response to Pre-Exam Formalities Notice	int13B.PDF	18068 3746bdb7e41b8ea89398e934afeebc17fba6b092	no	1
Warnings:					
Information:					
2	Oath or Declaration filed	int13C.PDF	48695 62578b2aedbfc433438a8820382ecce7282c5c7b	no	2
Warnings:					
Information:					
3	Fee Worksheet (SB06)	fee-info.pdf	30437 7a16da73afe1da63b2f3a38837160382965 5282c	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	97200		

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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.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
13/229,016	09/09/2011	1621	2792	H0024680-4511	46	4

CONFIRMATION NO. 8706

UPDATED FILING RECEIPT

91970
HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962

Date Mailed: 10/17/2011

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Applicant(s)

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HSUEH SUNG TUNG, Getzville, NY;
HALUK KOPKALLI, Staten Island, NY;

Assignment For Published Patent Application

HONEYWELL INTERNATIONAL INC., Morristown, NJ

Power of Attorney: None

Domestic Priority data as claimed by applicant

This appln claims benefit of 61/392,242 10/12/2010
and is a CIP of 13/195,429 08/01/2011
which is a CIP of 12/402,372 03/11/2009 PAT 8,013,194
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If Required, Foreign Filing License Granted: 09/20/2011

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 13/229,016**

Projected Publication Date: 01/26/2012

Non-Publication Request: No

Early Publication Request: No

Title

INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS

Preliminary Class

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Title 37, Code of Federal Regulations, 5.11 & 5.15

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PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 13/229,016

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	380
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	620
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	250
TOTAL CLAIMS (37 CFR 1.16(i))	46 minus 20 =	* 26			OR	x 60 =	1560
INDEPENDENT CLAIMS (37 CFR 1.16(h))	4 minus 3 =	* 1				x 250 =	250
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	3060

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

PTO/SB/08a (01-10)
Approved for use through 07/31/2012. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	13229016
Filing Date	2011-09-09
First Named Inventor	Selma Bektesevic
Art Unit	1621
Examiner Name	Not Yet Assigned
Attorney Docket Number	H0016235CON-4511

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	5396000		1995-03-07	Nappa et al.	
	2	5679875		1997-10-21	Aoyama et al.	
	3	6031141		2000-02-29	Mallikarjuna et al.	
	4	6548719		2003-04-15	Nair et al.	
	5	5672787		1997-09-30	Bielefeldt et al.	
	6	5714655		1998-02-03	Yamamoto et al.	
	7	4876405		1989-10-24	Gervasutti	
	8	5672803		1997-09-30	Smith et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	13229016
	Filing Date	2011-09-09
	First Named Inventor	Selma Bektesevic
	Art Unit	1621
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	H0016235CON-4511

	9	6734332		2004-05-11	Slaugh et al.	
	10	7230146		2007-06-12	Merkel et al.	
	11	6369284		2002-04-09	Nappa et al.	
	12	7560602		2009-07-14	Van Der Puy et al.	

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	Application Number	13229016
	Filing Date	2011-09-09
	First Named Inventor	Selma Bektesevic
	Art Unit	1621
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	H0016235CON-4511

	6	20110021849		2011-01-27	Avril et al.		
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	3	0982281	EP	A1	2000-03-01	Jp Agency Of Ind et al.		☐
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(71) Applicant *(for all designated States except US)*: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: NAPPA, Mario, Joseph [US/US]; 3 Oakridge Court, Newark, DE 19711 (US). RAO, V., N., Mallikarjuna [US/US]; 1 Georgetown Avenue, Wilmington, DE 19809 (US).

(74) Agent: HEISER, David, E.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

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(54) Title: THE CATALYTIC MANUFACTURE OF PENTAFLUOROPROPENES

(57) Abstract

A process is disclosed for the manufacture of a pentafluoropropene of the formula: $CFX{=}CYCF_3$ where X is selected from H and F and where Y is F when X is H and Y is H when X is F. The process involves contacting a hexafluoropropane of the formula: $CF_2XCHYCF_3$ at a temperature of from about 200 °C to 500 °C with a catalyst, optionally in the presence of an inert gas. Suitable catalysts include (1) catalysts of (a) at least one compound selected from the oxides, fluorides and oxyfluorides of magnesium, zinc and mixtures of magnesium and zinc, and optionally (b) at least one compound selected from the oxides, fluorides and oxyfluorides of aluminum; provided that the atomic ratio of aluminum to the total of magnesium and zinc in said catalyst is about 1:4, or less (e.g., 1:9), (2) lanthanum fluoride, (3) fluorided lanthanum oxide, (4) activated carbon, and (5) three–dimensional matrix carbonaceous materials.

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TITLE

THE CATALYTIC MANUFACTURE OF PENTAFLUOROPROPENES

FIELD OF THE INVENTION

This invention relates to processes for the production of pentafluoropropenes, and more particularly, to a catalytic process for the dehydrofluorination of hexafluoropropanes to pentafluoropropenes.

BACKGROUND

Hydrofluoropropenes are useful as materials for the preparation of fluoroplastics, fluoroelastomers and as monomers in the preparation of fluoropolymers.

European Patent Application EP 726 243 discloses a process for the manufacture of 1,2,3,3,3-pentafluoropropene (HFC-1225ye) by the dehydrofluorination of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea). The dehydrofluorination is done in the vapor phase in the presence of a trivalent chromium oxide or partly fluorinated trivalent chromium oxide catalyst.

U.S. Patent No. 5,396,000 discloses that HFC-236ea can be dehydrofluorinated to HFC-1225ye in the vapor phase in the presence of a catalyst selected from the group consisting of aluminum fluoride, fluorided alumina, metal supported on aluminum fluoride, metal supported on fluorided alumina, and mixtures thereof.

SUMMARY OF THE INVENTION

A process is provided for the manufacture of a pentafluoropropene of the formula $CFX{=}CYCF_3$ where X is selected from H and F and where Y is F when X is H and Y is H when X is F. The process comprises contacting a hexafluoropropane of the formula $CF_2XCHYCF_3$ at a temperature of from about 200°C to 500°C with a catalyst, optionally in the presence of an inert gas. The catalyst is selected form the group consisting of (1) catalysts of (a) at least one compound selected from the oxides, fluorides and oxyfluorides of magnesium, zinc and mixtures of magnesium and zinc, and optionally (b) at least one compound selected from the oxides, fluorides and oxyfluorides of aluminum; provided that the atomic ratio of aluminum to the total of magnesium and zinc in said catalyst is about 1:4, or less (e.g., 1:9), (2) lanthanum fluoride, (3) fluorided lanthanum oxide, (4) activated carbon, and (5) three-dimensional matrix carbonaceous materials.

DETAILED DISCUSSION

This invention provides a process for producing cis- and trans-1,2,3,3,3-pentafluoropropene (i.e., $CF_3CF{=}CHF$ or 1225ye) from 1,1,1,2,3,3-hexafluoropropane (i.e., $CF_3CHFCHF_2$, or HFC-236ea). A process is also provided for

producing 1,1,3,3,3-pentafluoropropene (i.e., $CF_3CH=CF_2$ or 1225zc) from 1,1,1,3,3,3-hexafluoropropane (i.e., $CF_3CH_2CF_3$, or HFC-236fa). HFC-236ea and HFC-236fa can be prepared by known art methods. For example, $CF_3CH_2CF_3$ can be prepared by contacting a mixture of hydrogen fluoride and 1,1,1,3,3,3-hexachloropropane (i.e., $CCl_3CH_2CCl_3$) in the vapor phase in the presence of a trivalent chromium catalyst as disclosed in U.S. Patent No. 5,414,165 and $CF_3CHFCHF_2$ can be prepared by hydrogenation of hexafluoropropene (i.e., $CF_3CF=CF_2$) in the the presence of a Pd/C catalyst.

In accordance with this invention, $CF_3CHFCHF_2$ is dehydrofluorinated to $CF_3CF=CHF$ and $CF_3CH_2CF_3$ is dehydrofluorinated to $CF_3CH=CF_2$ over a selected catalyst.

Suitable fluorided lanthanum oxide compositions can be prepared in any manner analogous to those known to the art for the preparation of fluorided alumina. For example, the catalyst composition can be prepared by fluorination of lanthanum oxide.

Suitable catalyst compositions can also be prepared by precipitation of lanthanum as the hydroxide which is thereafter dried and calcined to form an oxide, a technique well known to the art. The resulting oxide can then be pretreated as described herein.

The catalyst composition can be fluorinated to the desired fluorine content by treating with a fluorine-containing compound at elevated temperatures, e.g., at about 200°C to about 450°C. The pretreatment with a vaporizable fluorine-containing compound such as HF, SF_4, CCl_3F, CCl_2F_2, CHF_3, $CHClF_2$ or CCl_2FCClF_2 can be done in any convenient manner including in the reactor which is to be used for carrying out the dehydrofluorination reaction. By vaporizable fluorine-containing compound is meant a fluorine-containing compound which, when passed over the catalyst at the indicated conditions, will fluorinate the catalyst to the desired degree.

A suitable catalyst may be prepared, for example, as follows:

La_2O_3 is dried until essentially all moisture is removed, e.g., for about 18 hours at about 400°C. The dried catalyst is then transferred to the reactor to be used. The temperature is then gradually increased to about 400°C while maintaining a flow of N_2 through the reactor to remove any remaining traces of moisture from the catalyst and the reactor. The temperature is then lowered to about 200°C and the vaporizable fluorine-containing compound is passed through the reactor. If necessary, nitrogen or other inert gases can be used as diluents. The N_2 or other inert diluents can be gradually reduced until only the vaporizable fluorine-containing compound is being passed through the reactor. At this point the temperature can be increased to about 450°C and held at that temperature to

convert the La_2O_3 to a fluorine content corresponding to at least 80% LaF_3 by weight, e.g., for 15 to 300 minutes, depending on the flow of the fluorine containing compound and the catalyst volume.

Another suitable procedure for the catalyst preparation is to add ammonium hydroxide to a solution of $La(NO_3)_3 \cdot 6H_2O$. The ammonium hydroxide is added to the nitrate solution to a pH of about 9.0 to 9.5. At the end of the addition, the solution is filtered, the solid obtained is washed with water, and slowly heated to about 400°C, where it is calcined. The calcined product is then treated with a suitable vaporizable fluorine-containing compound as described above.

Carbon from any of the following sources are useful for the process of this invention; wood, peat, coal, coconut shells, bones, lignite, petroleum-based residues and sugar. Commercially available carbons which may be used in this invention include those sold under the following trademarks: Barneby & Sutcliffe™, Darco™, Nuchar™, Columbia JXN™, Columbia LCK™, Calgon PCB , Calgon BPL™, Westvaco™, Norit™ and Barnaby Cheny NB™. The carbon support can be in the form of powder, granules, or pellets, or the like.

Carbons include acid-washed carbons (e.g., carbons which have been treated with hydrochloric acid or hydrochloric acid followed by hydrofluoric acid). Acid treatment is typically sufficient to provide carbons which contain less than 1000 ppm of ash. Suitable acid treatment of carbons is described in U.S. Patent No. 5,136,113. The carbons of this invention also include three dimensional matrix porous carbonaceous materials. Examples are those described in U.S. Patent No. 4,978,649, which is hereby incorporated by reference herein in its entirety. Of note are three dimensional matrix carbonaceous materials which are obtained by introducing gaseous or vaporous carbon-containing compounds (e.g., hydrocarbons) into a mass of granules of a carbonaceous material (e.g., carbon black); decomposing the carbon-containing compounds to deposit carbon on the surface of the granules; and treating the resulting material with an activator gas comprising steam to provide a porous carbonaceous material. A carbon-carbon composite material is thus formed.

Other preferred catalysts include catalysts consisting essentially of magnesium fluoride, and catalysts consisting essentially of magnesium fluoride and at least one compound selected from the oxides, fluorides and oxyfluorides of aluminum.

A suitable catalyst may be prepared, for example, as follows:

Magnesium oxide is dried until essentially all water is removed, e.g., for about 18 hours at about 100°C. The dried material is then transferred to the reactor to be used. The temperature is then gradually increased to about 400°C

while maintaining a flow of nitrogen through the reactor to remove any remaining traces of moisture from the magnesium oxide and the reactor. The temperature is then lowered to about 200°C and a fluoriding agent such as HF or other vaporizable fluorine containing compounds such as SF_4, CCl_3F, CCl_2F_2, CHF_3 or CCl_2FCClF_2, optionally diluted with an inert gas such as nitrogen is passed through the reactor. The inert gas or nitrogen can be gradually reduced until only HF or other vaporizable fluorine containing compounds is being passed through the reactor. At this point the temperature can be increased to about 450°C and held at that temperature to convert the magnesium oxide to a fluoride content corresponding to at least 40% by weight, e.g., for 15 to 300 minutes, depending on the fluoriding agent flowrate and the catalyst volume. The fluorides are in the form of magnesium fluoride or magnesium oxyfluoride; the remainder of the catalyst is magnesium oxide. It is understood in the art that fluoriding conditions such as time and temperature can be adjusted to provide higher than 40 weight% fluoride-containing material.

Another suitable procedure for the catalyst preparation is to add ammonium hydroxide to a solution of magnesium nitrate and if present zinc nitrate and/or aluminum nitrate. The ammonium hydroxide is added to the nitrate solution to a pH of about 9.0 to 9.5. At the end of the addition, the solution is filtered, the solid obtained is washed with water, dried and slowly heated to 500°C, where it is calcined. The calcined product is then treated with a suitable fluorine-containing compound as described above.

Yet another procedure for the preparation of metal (i.e., magnesium optionally containing also zinc and/or aluminum) fluoride catalysts containing one or more metal fluorides is to treat an aqueous solution of the metal(s) halide(s) or nitrate(s) in deionized water was treated with 48% aqueous HF with stirring. Stirring is continued overnight and the slurry evaporated to dryness on a steam bath. The dried solid is then calcined in air at 400°C for about four hours, cooled to room temperature, crushed and sieved to provide material for use in catalyst evaluations.

The physical shape of the catalyst is not critical and may, for example, include pellets, powders or granules.

The catalytic dehydrofluorination of $CF_3CH_2CF_3$ and $CF_3CHFCHF_2$ is suitably conducted at a temperature in the range of from about 200°C to about 500°C and preferably from about 375°C to about 450°C. The contact time is typically from about 1 to about 450 seconds, preferably from about 10 to about 120 seconds.

The reaction pressure can be subatmospheric, atmospheric or superatmospheric. Generally, near atmospheric pressures are preferred. However,

the dehydrofluorination of $CF_3CH_2CF_3$ can be beneficially run under reduced pressure (i.e., pressures less than one atmosphere).

The reaction can be done in the presence of inert gases such as nitrogen and argon. It has been found that inert gases can be used to increase the dehydrofluorination (DHF) of $CF_3CH_2CF_3$ to $CF_3CH=CF_2$. Of note are processes where the mole ratio of inert gas to $CF_3CH_2CF_3$ fed to the dehydrofluorination is from about 5:1 to 1:1. Nitrogen is a preferred inert gas. Inert gases have essentially no effect on the DHF of $CF_3CHFCHF_2$ to $CF_3CF=CHF$.

Unreacted starting material can be recycled to the reactor for the production of additional $CF_3CF=CHF$ (1225ye) and $CF_3CH=CF_2$ (1225zc). The hydrofluoropropenes 1225ye and 1225zc may be recovered from the reaction product and any unreacted hydrofluoropropanes by conventional procedures such as distillation.

The process of this invention can be carried out readily in the vapor phase using well known chemical engineering practice.

Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention to its fullest extent. The following specific embodiments are to be construed as illustrative, and not as constraining the remainder of the disclosure in any way whatsoever.

EXAMPLES

Legend

236fa is $CF_3CH_2CF_3$	1225zc is $CF_3CH=CF_2$
236ea is $CF_3CHFCHF_2$	1225ye is cis- and trans-$CF_3CF=CHF$

CT is contact time

PREPARATION OF CATALYSTS

General Procedure for the Preparation of Magnesium Fluoride Containing Catalysts:

Unless stated otherwise, the following general procedure was followed for the preparation of magnesium fluoride catalysts containing one or more metal fluorides. An aqueous solution of the metal(s) halide(s) or nitrate(s) in deionized water was treated with 48% aqueous HF with stirring. Stirring was continued overnight and the slurry evaporated to dryness on a steam bath. The dried solid was then calcined in air at 400°C for about four hours, cooled to room temperature, crushed and sieved to provide a 12-20 mesh (1.68-0.84 mm) fraction which was used in catalyst evaluations.

Catalyst A - Fluorided Lanthanum Oxide

$La(NO_3)_3 \cdot 6H_2O$ (98.4 g) was dissolved in deionized water (1.5 L) in a 2 L beaker provided with an agitator. A solution (200 mL) of NH_4OH and deionized water (1/1, volume/volume) was added during a period of 10 minutes to the agitated solution. The pH of the solution was 9.5 after this addition. The slurry was filtered and dried in air at 125°C for about 18 hours, followed by calcination at 350°C in air for an additional 8 hours. The product (46.8 g) was compressed into wafers and screened. Particles in the 12 x 20 mesh (1.4 mm x 0.83 mm) range were used for the examples. The granulated catalyst precursor (15 mL, 17.6 g) was placed in a 5/8" (1.58 cm) Inconel® nickel alloy reactor heated in a fluidized sand bath. It was heated to 175°C in a flow of nitrogen (50 cc/min) at which time HF flow (50 cc/min) was also started through the reactor. As the initial exotherm monitored by an internal thermocouple subsided (2-3 hours), nitrogen flow was decreased to 20 cc/min and HF flow increased to 80 cc/min. The reactor temperature was gradually increased to 400°C during a 3-4 hour period and maintained at 400°C for an additional 30 minutes. At the end of this period the reactor was brought to the desired operating temperature for catalyst evaluation.

Catalyst B - MgF_2

Following the general procedure described above for the preparation of fluorinated catalysts, a MgF_2 catalyst was prepared from 150.0 g of $Mg(NO_3)_2 \cdot 6H_2O$, 500 mL deionized water and 75 mL 48% aqueous HF.

Catalyst C - MgF_2/AlF_3 (43:1):

Following the general procedure described above for the preparation of fluorinated catalysts, a MgF_2/AlF_3 catalyst having a nominal magnesium to aluminum atomic ratio of 43:1 was prepared from 251.28 g $Mg(NO_3)_2 \cdot 6H_2O$, 7.50 g $Al(NO_3)_3 \cdot 9H_2O$ and 100 mL 48% aqueous HF.

Catalyst D - MgF_2/AlF_3 (9:1):

Following the general procedure described above for the preparation of fluorinated catalysts, a MgF_2/AlF_3 catalyst having a nominal magnesium to aluminum atomic ratio of 9:1 was prepared from 237.6 g $Mg(NO_3)_2 \cdot 6H_2O$, 34.76 g $Al(NO_3)_3 \cdot 9H_2O$ and 120 mL 48% aqueous HF.

Catalyst E-H

Commercial samples of acid-washed coconut shell carbon were used.

Catalyst I

Porous carbonaceous material prepared substantially as described in U.S. Patent No. 4,9789,649 was used.

Catalyst J

A commercial sample of coconut shell carbon (not acid-washed) was used.

Catalyst K - Fluorided Magnesia

A commercial sample of magnesium oxide which was pelletized and ground to 12/20 mesh (1.68/0.84 mm) was heated to 200°C for two hours while purging with nitrogen (50 sccm, 8.3 x 10^{-7} m^3/s). The nitrogen was continued at 50 sccm (8.3 x 10^{-7} m^3/s), and the catalyst contacted with HF (50 sccm, 8.3 x 10^{-7} m^3/s) for 15 minutes. The HF flow was raised to 80 sccm (1.3 x 10^{-6} m^3/s) and the nitrogen flow reduced to 20 sccm (3.3 x 10^{-7} m^3/s) for 25 minutes. The temperature was raised to 250°C for 75 minutes, 300°C for 75 minutes, 350°C for 75 minutes, and 400°C for 75 minutes while maintaining the flows of HF and nitrogen to provide a fluorided magnesia catalyst.

Catalyst L - Fluorided Alumina

A commercial sample of gamma-alumina extrudate (10.6 g, 15 mL, 1/12", 2.1 mm) was dried at 110°C in air for 18 hours in a 5/8" (1.58 cm) Inconel® nickel alloy reactor heated in a fluidized sand bath. The temperature was raised to 200°C and HF and nitrogen (1:4 molar ratio) were passed through the alumina. The nitrogen flow was decreased with time until neat HF was being passed through the reactor. At this point the temperature was gradually raised to 450°C and maintained there for 30 minutes. The fluorine content of the fluorided alumina corresponded to an AlF_3 content of at least 50%.

Catalyst M - Chromium Oxide

A commercial sample (39.9 g, 30 mL) of chromium oxide (Cr_2O_3) was used.

Table 1 lists the catalyst, its weight and volume and the examples for which the listed catalyst was used.

EXAMPLES 1-9

$$CF_3CHFCHF_2 \rightarrow CF_3CF{=}CHF + HF$$

A 15 in. (38.1 cm) x 3/8 in (0.95 cm) Hastelloy™ nickel alloy tube was filled with the amounts of catalyst shown in Table 1. The reactor was heated to the temperatures recorded in Table 2. The flow of 1,1,1,2,3,3-hexafluoropropane was begun to the reactor with the contact times shown. The dehydrofluorination results (mole %) are shown in Table 2.

TABLE 1

Ex.	Cat.	Wt. (g)	Vol. (mL)
1, 10	A	17.6	15
2	B	8.9	10
3, 11	C	8.4	10
4, 12	D	8.0	10
5	E	8.3	20
6	F	7.4	20
7	G	7.3	20
8	H	8.7	20
9	I	10	20
13	H	4.7	10
14	I	5.3	10
15	J	6.2	10
16	K	10.4	13
A, B	L	10.6	15
C	M	39.9	30

TABLE 2

Ex.	Cat.	T (°C)	CT	%236ea	%1225ye
1	A	350	60	99.5	0.3
		400	60	98.0	1.9
		450	60	92.9	7.0
		500	60	83.7	16.1
2	B	350	120	99.9	0.1
		400	120	99.4	0.5
		450	120	97.8	2.2
3	C	350	120	96.3	3.6
		400	120	89.7	10.3
		425	120	83.8	16.2
		450	120	75.5	24.5
		450	60	85.2	14.7
4	D	350	120	83.2	16.8
		400	120	64.4	35.6
		450	120	42.2	57.8
5	E	350	120	99.0	0.9
		375	120	97.1	2.7
		400	120	88.2	11.7

		425	120	35.8	63.2
		450	120	7.5	80.1
6	F	350	120	98.9	1.0
		375	120	97.2	2.7
		400	120	86.1	13.3
		425	120	31.6	64.9
		450	120	9.9	77.8
7	G	350	120	99.8	0.1
		400	120	79.8	20.2
		425	120	36.6	58.6
8	H	350	120	99.5	0.5
		375	120	83.2	16.8
		400	120	60.9	39.0
		425	120	29.1	69.2
		450	120	10.8	73.1
9	I	325	120	93.1	6.9
		350	120	84.1	15.9
		375	120	67.6	32.4
		400	120	48.1	51.9

COMPARATIVE EXAMPLE A

The same apparatus and procedure as used for Examples 1-9 were used for comparative example A. The results are shown in Table A.

TABLE A

Ex.	Cat.	T (°C)	CT	%236ea	%1225ye
A	L	325	30	69.4	28.5
		350	60	46.7	52.3
		400	60	8.3	89.9

EXAMPLES 10-16

$CF_3CH_2CF_3 \rightarrow CF_3CH{=}CF_2 + HF$

The same apparatus and procedure as used for Examples 1-9 were used for Examples 10-15. The results are shown in Table 3. Examples 10-12 are reported in mole%; Examples 13-15 are reported in area%.

TABLE 3

Ex.	Cat.	T (°C)	CT	[A]:[B][a]	%236fa	%1225zc
10	A	350	60		98.5	1.3
		375	60		96.8	3.1
		450	60		84.7	15.2
		500	60		56.8	42.7
11	C	350	120		91.3	8.7
		400	120		78.1	21.8
		450	120		55.1	44.7
		450	60		47.1	52.6
		450	30		49.3	50.4
12	D	350	120		91.2	8.7
		400	120		78.3	21.6
		400	60		71.5	28.4
		450	120		54.2	45.6
		450	60		45.5	54.2
13	H	350	60	-	94.1	5.8
		350	120	-	91.8	8.2
		350	120	1:2	96.3	3.7
		350	120	1:1	95.7	4.2
		375	60	-	86.5	13.4
		375	120	-	87.9	11.9
		375	120	1:2	79.9	20.1
		375	120	1:1	95.7	4.2
		400	60	-	81.9	17.7
		400	120	-	85.0	14.1
		400	120	1:2	72.7	26.7
		400	120	1:1	76.7	22.6
		425	40	-	74.4	25.0
		425	120	-	76.2	21.2
		425	120	1:2	63.2	35.3
		425	120	1:1	67.3	31.2
14	I	350	60	-	96.1	3.8
		350	120	-	94.6	5.4
		350	120	1:1	95.4	4.6
		375	60	-	93.2	6.7
		375	120	-	90.3	9.5
		375	120	1:2	95.7	4.3

		375	120	1:1	94.4	5.6
		400	60	-	90.2	9.7
		400	40	-	93.8	6.1
		400	120	-	91.3	8.4
		400	120	1:2	96.2	3.8
		400	120	1:1	93.7	6.2
		425	40	-	74.6	25.3
		425	120	-	75.2	24.6
		425	120	1:2	67.1	32.8
		425	120	1:1	68.9	31.0
15	J	350	60	-	93.1	6.7
		350	120	-	91.8	8.0
		350	120	1:2	93.5	6.5
		350	120	1:1	91.7	8.2
		375	60	-	86.2	13.6
		375	120	-	86.9	12.8
		375	120	1:2	80.3	19.6
		375	120	1:1	81.7	18.2
		400	60	-	80.0	19.7
		400	120	-	79.6	20.1
		400	120	1:2	71.6	28.1
		400	120	1:1	75.6	23.6
		425	40	-	73.8	25.7
		425	120	-	75.4	22.3
		425	120	1:2	63.3	35.4
		425	120	1:1	67.0	31.7
16	K	421	60	1:1	81.4	16.8

[a] [A]:[B] is the molar ratio of 236fa to nitrogen in the initial reactor feed. No nitrogen was used for the runs where there is no entry in this column.

COMPARATIVE EXAMPLES B AND C

The same apparatus and procedure as used for Examples 1-9 were used for comparative examples B and C. The results are shown in Table B.

TABLE B

Ex.	Cat.	T (°C)	CT	%236fa	%1225zc
B	L	300	30	96.9	0.9
		350	30	90.5	7.1
C	M	350	30	92.7	7.1
		350	60	89.0	10.8
		350	30	88.4	11.5
		350	15	87.1	12.7
		400	15	74.5	24.8
		400	15	83.3	16.2
		400	10	87.9	11.9

CLAIMS

1. A process for the manufacture of a pentafluoropropene of the formula $CFX=CYCF_3$ where X is selected from H and F and where Y is F when X is H and Y is H when X is F, comprising:

contacting a hexafluoropropane of the formula $CF_2XCHYCF_3$ at a temperature of from about 200°C to 500°C with a catalyst, optionally in the presence of an inert gas; said catalyst being selected form the group consisting of (1) catalysts of (a) at least one compound selected from the oxides, fluorides and oxyfluorides of magnesium, zinc and mixtures of magnesium and zinc, and optionally (b) at least one compound selected from the oxides, fluorides and oxyfluorides of aluminum; provided that the atomic ratio of aluminum to the total of magnesium and zinc in said catalyst is about 1:4, or less, (2) lanthanum fluoride, (3) fluorided lanthanum oxide, (4) activated carbon, and (5) three-dimensional matrix carbonaceous materials.

2. The process of Claim 1 wherein $CF_3CH_2CF_3$ is dehydrofluorinated to provide $CF_3CH=CF_2$.

3. The process of Claim 2 wherein an inert gas is fed to the dehydrofluorination in a mole ratio to $CF_3CH_2CF_3$ of from about 5:1 to 1:1.

4. The process of Claim 3 wherein the inert gas is nitrogen.

5. The process of Claim 2 wherein the dehydrofluorination is run under reduced pressure.

INTERNATIONAL SEARCH REPORT

Interna I Application No
PCT/US 98/00429

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C17/25 C07C19/08

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)
IPC 6 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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 644 173 A (DAIKIN IND LTD) 22 March 1995 see page 2, line 39-58 see page 6, line 51 - page 7, line 17 see claims 1,2	1-5
P,X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 007, 31 July 1997 & JP 09 067281 A (DAIKIN IND LTD), 11 March 1997, see abstract	1-5
A	EP 0 726 243 A (DAIKIN IND LTD) 14 August 1996 cited in the application see abstract	1-5

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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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

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1

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Interna l Application No
PCT/US 98/00429

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 396 000 A (NAPPA MARIO J ET AL) 7 March 1995 cited in the application see abstract -----	1-5

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Interna al Application No
PCT/US 98/00429

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(71) Applicants:
- **JAPAN as Represented by DIRECTOR GENERAL OF AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOGY**
  Chiyoda-ku, Tokyo 100-0013 (JP)
- **Nippon Zeon Co., Ltd.**
  Tokyo 100-0005 (JP)

(72) Inventors:
- **SEKIYA, Akira,**
  Ibaraki 305-8565 (JP)
- **YAMADA, Toshirou,**
  Research & Development Center,
  Kawasaki-shi, Kanagawa 210-0863 3 (JP)
- **URUMA, Takashi,**
  Research & Development Center,
  Kawasaki-shi Kanagawa 210-0863 863 (JP)
- **SUGIMOTO, Tatsuya,**
  Research & Development Center,
  Kawasaki-shi Kanagawa 210-0863 (JP)

(74) Representative:
Calamita, Roberto
Frank B. Dehn & Co.,
European Patent Attorneys,
179 Queen Victoria Street
London EC4V 4EL (GB)

(54) FLUORINATED, SATURATED HYDROCARBONS

(57) A fluorinated saturated hydrocarbon which is an acyclic or cyclic fluorinated saturated hydrocarbon characterized by comprising less than 95 mol% of a trihydrofluorinated saturated hydrocarbon represented by the following formula (I)

$$Rf_1\text{-}R_1\text{-}Rf_2 \quad (I)$$

(wherein R_1 represents a carbon chain in which CHF and CH_2 are bound, Rf_1 and Rf_2 each represents a perfluoroalkyl group, a fluorine atom or a hydrogen atom, at least one thereof is a perfluoroalkyl group, and further Rf_1 and Rf_2 may be bound to each other to form a ring by a perfluoroalkylene chain)

and the balance of a tetrahydrofluorinated saturated hydrocarbon having the same carbon number and the same carbon structure as the trihydrofluorinated saturated hydrocarbon, as represented by the following formula (II)

$$Rf_1\text{-}R_2\text{-}Rf_2 \quad (II)$$

(wherein R_2 represents a carbon chain in which CH_2 and CH_3 are bound, and Rf_1 and Rf_2 are as defined above)

is provided as a fluorinated saturated hydrocarbon containing, in a high proportion, trihydrofluorocarbon which is excellent especially in the chemical stability and high in the safety for living bodies among hydrofluorocarbons (HFC) known to have zero ozone depletion potential and to have a small global warming potential.

EP 0 982 281 A1

Description

Technical Field:

[0001] The invention of this application relates to fluorinated saturated hydrocarbons. More specifically, the invention of this application relates to fluorinated saturated hydrocarbons, which are useful as substitute compounds of CFC (chlorofluorocarbon), HCFC (hydrochlorofluorocarbon), PFC (perfluoro compound), and chlorine-type solvents, which have been widely used as detergents, foaming agents, refrigerants, and the like. The compounds described in the invention of this application have less influence on the global environment, show less toxicity to human bodies, and are chemically stable. The invention of this application also relates to a process for producing the above compounds, and compositions thereof.

Background of the Invention:

[0002] As an industrial method for washing various materials, products composed mainly of CFC 113 or 1,1,1-trichloroethane which are incombustible, low in toxicity, and excellent in stability have been widely used. However, it has been identified that various CFCs, 1,1,1-trichioroethane, carbon tetrachloride and the like destroy the stratospheric ozone layer. In view of the protection of the ozone layer, the production of CFC 113, 1,1,1-trichloroethane and the like has been completely abolished worldwide since the end of 1995, and regulations have been set on their use.

[0003] As substitutes of CFC 113 and the like, hydrochlorofluorocarbons such as HCFC 225 and HCFC 141b have been proposed. However, since these compounds are, though slightly, also destructive to the ozone layer, a time limit has been set in their use. Further, chlorinated solvents such as methylene chloride, trichloroethylene, perchloroethylene and the like have also been problematic regarding their safety (carcinogenicity and intoxication), and various regulations have been already set or are being studied.

[0004] Further, various fluorine type compounds which do not contain chlorine atoms that cause the destruction of the ozone layer, and can maintain noncombustibility, safety and such merits as mentioned above, have been synthesized. For example, a product composed mainly of perfluorocarbons such as perfluoro-n-heptane (WO 92-03205 and the like), a product composed mainly of acyclic hydrofluorocarbon (WO 95-06693, JP-W-6-501949 and the like), a product composed mainly of specific acyclic hydrofluorocarbons (WO 95-05448) and the like are mentioned.

[0005] These perfluorocarbons and hydrofluorocarbons were preferable because there is no worry for the destruction of the ozone layer and detergency with good finish is exhibited by using the same as such or along with organic solvents. However, these compounds each had problems that needed to be improved. For example, perfluorocarbons have high global warming coefficient, and there is fear that new problems on the preservation of the global environment might occur. Further, with respect to acyclic or cyclic hydrofluorocarbons, various structures have been proposed, but have problems in their structures. For example, compounds having -CH_2CH_2- bonds, with 4 or 5 carbon atoms, and a boiling point in the region suitable for detergents or solvents, were defected in that they are combustible.

[0006] Accordingly, an object of the invention of this application is to provide, upon improving the defects of such hydrofluorocarbons known so far, fluorinated saturated hydrocarbons which are excellent as detergents, and excellent in their non-combustibility and their stability in the presence of water, which can construct new detergents and the like, and are easy to produce, a process for producing the same, and compositions thereof.

Disclosure of the Invention:

[0007] The invention of this application is to provide, as a product to solve the above-mentioned problems, an acyclic or cyclic fluorinated saturated hydrocarbon characterized by comprising less than 95 mol% of a trihydrofluorinated saturated hydrocarbon (A) represented by the following formula (I)

$$Rf_1\text{-}R_1\text{-}Rf_2 \qquad (I)$$

(wherein R_1 represents a carbon chain in which CHF and CH_2 are bound, Rf_1 and Rf_2 each represents a perfluoroalkyl group, a fluorine atom or a hydrogen atom, at least one thereof is a perfluoroalkyl group, and further Rf_1 and Rf_2 may be bound to each other to form a ring by a perfluoroalkylene chain)

and the balance of a tetrahydrofluorinated saturated hydrocarbon (B) having the same number of carbons and the same carbon structure as the trihydrofluorinated saturated hydrocarbon (A), as represented by the following formula (II)

$$Rf_1\text{-}R_2\text{-}Rf_2 \qquad (II)$$

(wherein R_2 represents a carbon chain in which CH_2 and CH_3 are bound, and Rf_1 and Rf_2 are as defined above).

[0008] Further, the invention of this application also provides a process for producing a fluorinated saturated hydrocarbon comprising a compound represented by the following formula (III)

$$Rf_1\text{-}R_1\text{-}Rf_2 \qquad (III)$$

(wherein R_1 represents a carbon chain in which CHX and CH_2 are bound, X represents a hydrogen atom or a fluorine atom, Rf_1 and Rf_2 each represent a perfluoroalkyl group, a fluorine atom or a hydrogen atom, at least one thereof is a perfluoroalkyl group, and further Rf_1 and Rf_2 may be bound to each other to form a ring by a perfluoroalkylene chain) and a compound represented by the following formula (IV)

$$Rf_1\text{-}R_2\text{-}Rf_2 \quad (IV)$$

(wherein R_2 represents a carbon chain in which CHX and CHF are bound, and X, Rf_1 and Rf_2 are as defined above),

characterized in that when a fluorinated, unsaturated hydrocarbon represented by the following formula (V)

$$Rf_1\text{-}R_3\text{-}Rf_2 \quad (V)$$

(wherein R_3 represents a carbon chain of -CX=CF-, X represents a hydrogen atom or a fluorine atom, Rf_1 and Rf_2 each represent a perfluoroalkyl group, a fluorine atom or a hydrogen atom, at least one thereof is a perfluoroalkyl group, and further Rf_1 and Rf_2 may be bound to each other to form a ring by a perfluoroalkylene chain)

is catalytically reduced under hydrogen using a noble metal catalyst, the proportions of the fluorinated saturated hydrocarbon of formula (III) and the fluorinated saturated hydrocarbon of formula (IV) are controlled by changing the polarity of the component other than the substrate starting material of the reaction system (claim 2).

[0009] Still further, the invention of this application provides a composition of a fluorinated saturated hydrocarbon which is a composition containing the above-mentioned fluorinated saturated hydrocarbons (A) and (B), characterizing in that at least one type of an organic solvent having a boiling point of at least 25°C and at most 250°C is contained along with the fluorinated saturated hydrocarbon compounds.

Best Mode for Carrying Out the Invention:

[0010] The fluorinated saturated hydrocarbon of this invention is characterized in that it is an acyclic or cyclic fluorinated hydrocarbon in which the trihydrofluorinated saturated hydrocarbon (A) of formula (I) and the tetrahydrofluorinated saturated hydrocarbon (B) of formula (II) co-exist in specific proportions. In this case, the co-existing proportions of the fluorinated saturated hydrocarbons (A) and (B) are

(A): less than 95 mol%
(B): balance,

and the fluorinated saturated hydrocarbon (B) as the balance is usually present in an amount of 5 mol% or more based on the total amount containing unavoidable impurities.

[0011] The reason that the proportions of the fluorinated saturated hydrocarbons (A) and (B) are as mentioned above is that according to the invention of this application, the fluorinated hydrocarbon of this invention is provided by a specific process described later in this application, and as a content of a detergent or the like, the fluorinated saturated hydrocarbon of this invention is introduced as a novel product.

[0012] The proportion of the trihydrofluorinated hydrocarbon (A) is less than 95 mol%, generally 10 mol% or more, preferably 50 mol% or more, more preferably 70 mol% or more, further preferably 80 mol% or more. The higher the proportion of the trihydrofluorinated hydrocarbon (A), the more the fluorinated saturated hydrocarbon of this invention becomes non-combustible.

[0013] The fluorinated saturated hydrocarbons (A) and (B) are acyclic or cyclic fluorinated hydrocarbons. The fluorinated saturated hydrocarbons (A) and (B) are preferably cyclic. The number of carbon atoms in the fluorinated hydrocarbons is usually between 3 and 10, preferably between 4 and 6, and most preferably 5. Specific compounds of the fluorinated saturated hydrocarbon (A) having the trihydrofluorocarbon chain include, for example, acyclic trihydrofluorinated saturated hydrocarbons such as 1,1,1,2,3-pentafluoropropane, 1,1,1,3,3-pentafluoropropane, 1,1,1,2,4,4,4-heptafluoro-n-butane, 1,1,1,2,2,3,5,5,5-nonafluoro-n-pentane, 1,1,1,2,2,4,5,5,5-nonafluoro-n-pentane, 1,1,1,2,2,3,3,4,6,6,6-undecafluoro-n-hexane, 1,1,1,2,2,3,3,5,6,6,6-undecafluoro-n-hexane, 1,1,1,2,2,4,5,5,6,6,6-undecafluoro-n-hexane, 1,1,1,2,2,3,3,5,6,6,7,7,7-tridecafluoro-n-heptane, 1,1,1,2,2,3,3,5,6,6,7,7,8,8,8-pentadecafluoro-n-octane, 1,1,1,2,2,3,3,5,6,6,7,7,8,8,9,9,10,10,10-nonadecafluoro-n-decane and the like; cyclic trihydrofluorinated saturated hydrocarbons such as 1,1,2,2,3-pentafluorocyclobutane, 1,1,2,2,3,3,4-heptafluorocyclopentane, 1,1,2,2,3,3,4,4,5-nonafluorocyclohexane, 1,1,2,2,3,3,4,4,5,5,6-undecafluorocycloheptane, 1,1,2,2,3,3,4,4,5,5,6,6,7-tridecafluorocyclooctane, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8-pentadecafluorocyclononane and the like; and so forth. Of these, 1,1,1,2,2,3,5,5,5-nonafluoro-n-pentane, 1,1,1,2,2,4,5,5,5-nonafluoro-n-pentane and 1,1,2,2,3,3,4-heptafluorocyclopentane are mentioned preferably, and 1,1,2,2,3,3,4-heptafluorocyclopentane (HFCPA) is mentioned as especially preferable.

[0014] In this invention, the tetrahydrofluorinated saturated hydrocarbon (B) having the same number of carbons and the same carbon structure as the trihydrofluorinated saturated hydrocarbon (A) co-exists. For example, it is shown that 1,1,2,2,3,3-hexafluorocyclopentane co-exists with 1,1,2,2,3,3,4-heptafluorocyclopentane (HFCPA) mentioned above.

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[0015] With respect to the fluorinated saturated hydrocarbons of this invention, the boiling point is preferably at least 25°C and at most 150°C, especially preferably at least 50°C and at most 100°C when it is used as constituting a detergent.

[0016] The fluorinated hydrocarbon of this invention is excellent in detergency, is highly non-combustible, is excellent in stability under the presence of water, and the production thereof is easy.

[0017] Thus, the process for producing the fluorinated hydrocarbon of the invention of this application is described.

[0018] The process for producing the fluorinated saturated hydrocarbon of this invention, which contain the fluorinated hydrocarbon compounds represented by formulas (III) and (IV) such as the fluorinated hydrocarbons (A) and (B) mentioned above, is quite unique. For example, the formation of 1H,1H,2H-heptafluorocyclopentane or the like which is a trihydro compound has been so far observed during the reaction of hydrogenating perfluorocyclopentene in the presence of palladium-alumina, and it is disclosed that the main product of this reaction is 1H,2H-octafluorocyclopentane (J. Chem. Soc., C.548 (1968)). Only 10% of heptafluorocyclopentane (HFCPA) having a trihydrofluorocarbon chain was reportedly obtained, and further, was difficult to separate from octaflurocyclopentane (OFCPA) by distillation.

[0019] Moreover, according to the official gazette of JP-B-5-148171, when 1,1,1,2,2,3,4,5,5,5-decafluoropentane is produced by hydrogenating decafluoropentene-2 using palladium supported on carbon, alumina, or the like as a catalyst, by products such as 1,1,1,2,2,4,5,5,5-nonafluoropentane, 1,1,1,2,2,3,5,5,5-nonafluoropentane, 1,1,1,2,2,5,5,5-octafluoropentane and the like were produced in large amounts. However, it was reportedly difficult to separate these byproducts from the desired product by the process of distillation.

[0020] That is, providing fluorinated saturated hydrocarbons containing heptafluorocyclopentane (HFCPA) and the like which contain trihydrofluorocarbon chains in high proportions has not been industrially realized so far.

[0021] Meanwhile, in the process of this invention, an acyclic or cyclic fluorinated, unsaturated hydrocarbon having the unsaturated fluorocarbon chain as represented by formula (V) is used as a substrate starting material, and is catalytically reduced in a hydrogen atmosphere using a noble metal catalyst. Here, the proportions of the fluorinated saturated hydrocarbon of formula (III) and the fluorinated saturated hydrocarbon of formula (IV) are controlled by changing the polarity of the component in the reaction system, other than the substrate starting material.

[0022] That is, in the method of this invention, the fluorinated saturated hydrocarbon of formula (III) can be produced more selectively by making the polarity of the component other than the substrate starting material of the reaction system high. On the other hand, the fluorinated saturated hydrocarbon of formula (IV) can be produced more selectively by making the polarity of the component other than the substrate starting material of the reaction system low. For example, when an unsaturated fluorinated hydrocarbon having carbon chains of -CF=CF-, as in formula (V), is the starting material, where the symbol X represents a fluorine atom (F), a trihydrofluorinated saturated hydrocarbon having a carbon chain of $-CHF-CH_2-$ as the fluorinated saturated hydrocarbon of formula (III) can be produced by making the polarity of the component other than the substrate starting material of the reaction system high. Meanwhile, when an unsaturated, fluorinated hydrocarbon having a carbon chain of -CH=CF- in which the symbol X in formula (V) represents a hydrogen atom (H) is used as a starting material, a trihydrofluorinated saturated hydrocarbon having a carbon chain of $-CHF-CH_2-$ as the fluorinated saturated hydrocarbon of formula (IV) can selectively be produced by making the polarity of the component other than the substrate starting material of the reaction system low.

[0023] In the fluorinated, unsaturated hydrocarbon represented by formula (V) as the substrate starting material, the carbon number is usually between 3 and 10, preferably between 4 and 6, most preferably 5. Further, the fluorinated, unsaturated hydrocarbon is acyclic or cyclic, preferably cyclic. The starting material can be obtained depending on various methods and the like. For example, the synthesis thereof can be conducted by a method described in the official gazette of JP-A-8-12608 or the like.

[0024] Here, the component other than the substrate starting material of the reaction system refers to high-polarity compounds or low-polarity compounds added to the substrate starting material, or impurities accompanying the substrate starting material.

[0025] That is, in order to make high the polarity of the component other than the substrate starting material of the reaction system, it is advisable to use, for example, a starting material containing the fluorinated, unsaturated hydrocarbon represented by formula (V) as the substrate starting material, and a high-polarity compound or a starting material obtained by removing the low-polarity compounds from the impurities accompanying the substrate starting material to increase the proportion of the high-polarity compounds in impurities. Further, in order to make the polarity of the component other than the substrate starting material of the reaction system low, it is advisable to use, for example, a starting material containing the fluorinated, unsaturated hydrocarbon represented by formula (V) and a low-polarity compound or a starting material obtained by removing the high-polarity compounds from impurities accompanying the substrate starting material to increase the proportion of the low-polarity compound in impurities. Here, the polarity of the compound used can be defined by a dielectric constant as described in, for example, Organic Solvents (John A. Riddick, et al (1986), John Wiley &

Sons, Inc. 4th Edition), Kagaku Binran (Kisohen II, II-498 to II-501) or the like.

[0026] Accordingly, a process in which a trihydrofluorinated saturated hydrocarbon in which the symbol X of formula (III) represents a fluorine atom, is selectively produced by making the polarity of the component other than the substrate starting material of the reaction system high, is first described.

[0027] In this case, a compound in which the symbol X in formula (V) represents a fluorine atom is used as a starting material. Specific examples thereof include, for example, acyclic fluorinated, unsaturated hydrocarbons such as 1,1,1,2,3,3-hexafluoropropene, 1,1,1,2,3,4,4,4-octafluoro-n-butene, 1,1,1,2,2,3,4,5,5,5-decafluoro-n-pentene, 1,1,1,2,2,3,3,4,5,6,6,6-dodecafluoro-n-hexene and the like; cyclic fluorinated, unsaturated hydrocarbons such as 1,1,2,2,3,4-hexafluorocyclobutene, 1,1,2,2,3,3,4,5-octafluorocyclopentene, 1,1,2,2,3,3,4,4,5,6-decafluorocyclohexene and the like; and so forth. Of these, 1,1,2,2,3,4,5,5,5-decafluoro-n-pentene and 1,1,2,2,3,3,4,5-octafluorocyclopentene are mentioned preferably, and 1,1,2,2,3,3,4,5-octafluorocyclopentene is mentioned especially preferably.

[0028] The low-polarity compound of which the amount has to be adjusted to a small amount relative to the substrate, in order to make the polarity of the component other than the substrate starting material of the reaction system high includes, for example, paraffins such as n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane and the like, and structural isomers thereof; naphthenes such as cyclopentane, cyclohexane, methylcyclohexane and the like; aromatics such as benzene, toluene, o-xylene, m-xylene, p-xylene and the like, and analogues thereof; mineral oils such as a machine oil, a cutting oil, a printing ink oil, a vacuum pump oil and the like; chlorofluorocarbons such as chlorononafluorocyclopentane, chloroheptafluorocyclopentene and the like; and so forth. The content of these low-polarity compounds is 1% by weight or less, preferably 0.5% by weight or less, more preferably 0.1% by weight or less.

[0029] The low-polarity compound to be noted especially is paraffins, naphthenes and aromatics.

[0030] The low-polarity compound accompanying the substrate starting material can reduce the content in the starting material by means such as adsorption treatment using an adsorbent and the like. For example, the treatment with an adsorbent such as an activated carbon or the like is a typical one.

[0031] And in the process of this invention, it is also important that the substrate starting material is mixed with the high-polarity compound. As the high-polarity compound, there are water, alcohols, polyhydric alcohols, monoethers of these polyhydric alcohols, amides, sulfoxides and the like. Specific examples include, for example, alcohols such as methyl alcohol, ethyl alcohol, n-propyl alcohol, n-butyl alcohol, n-pentyl alcohol and the like, and their structural isomers ; polyhydric alcohols such as ethylene glycol, glycerol, diethylene glycol, diethylene glycol monomethyl ether and the like, and monoethers of these polyhydric alcohols; amides such as N,N-dimethylacetamide, N,N-dimethylformamide and the like; sulfoxides such as dimethyl sulfoxide and the like; and so forth. The mixing proportion of these high-polarity compounds is not particularly limited, and they may be used as additives or solvents. Further, these high-polarity compounds may be used either alone or in mixtures of two or more.

[0032] Usually, the mixing proportion is between 0.1 and 20% by weight based on the substrate starting material. It is preferably between 0.1 and 15% by weight, more preferably between 0.5 and 15% by weight.

[0033] Next, a process for producing the fluorinated saturated hydrocarbon of formula (IV) more selectively by making the polarity of the component other than the substrate starting material of the reaction system low is described.

[0034] In this case, it is important that the low-polarity compound is contained in the starting material. Examples of the low-polarity compound are the same as the above-mentioned. It is advisable that the proportion of these low-polarity compounds is between 0.1 and 20% by weight. It is preferably between 0.1 and 15% by weight, more preferably between 0.5 and 15% by weight. Further, these low-polarity compounds may be used either alone or in admixture of two or more.

[0035] Further, in this invention, it is also important to reduce the content of the high-polarity impurities relative to the starting material. Examples of the high-polarity compound are the same as the above-mentioned. The content of these high-polarity impurities has to be 1% by weight or less in the starting material. It is preferably 0.5% by weight or less, more preferably 0.1% by weight or less.

[0036] With respect to the high-polarity compound accompanying the substrate starting material, the content in the starting material can be decreased by means such as adsorption treatment using an adsorbent or the like. For example, treatment with an adsorbent such as activated alumina or the like is a typical one.

[0037] The trihydrofluorinated saturated hydrocarbon in which the symbol X in formula represents a hydrogen atom is selectively produced as the fluorinated saturated hydrocarbon of formula (IV) by making low the component other than the substrate starting material of the reaction system. In this case, the starting material is a compound represented by the formula (V), in which X is a hydrogen atom. Examples include acyclic fluorinated, unsaturated hydrocarbons such as 1,1,1,2,3-pentafluoropropene, 1,1,1,3,3-pentafluoropropene, 1,1,1,2,2,3,5,5,5-nonafluoro-n-pentene, 1,1,1,2,2,3,3,4,6,6,6-undecafluoro-n-hexene and the like; and cyclic fluorinated, unsaturated hydrocarbons such as 1,1,2,2,3-pentafluorocyclobutene,

1,1,2,2,3,3,4-heptafluorocyclopentene and the like. Of these, 1,1,2,2,3,3,4-heptafluorocyclopentene is mentioned especially preferably.

[0038] The fluorinated saturated hydrocarbon containing the trihydrofluorinated hydrocarbon (A) and the tetrahydrofluorinated saturated hydrocarbon (B) in this invention corresponds to the case in which the fluorinated unsaturated hydrocarbon of the following formula where the symbol X represents a hydrogen atom, is used as the starting compound of formula (V), as mentioned above.

$$Rf_1\text{-}CH{=}CF\text{-}Rf_2$$

[0039] The trihydrofluorinated saturated hydrocarbon (A) can be controlled to a proportion of less than 95 mol% while coexisting with the tetrahydrofluorinated saturated hydrocarbon (B).

[0040] As the noble metal catalyst in the process of this invention, a noble metal supported on a carrier is usually used. The noble metal mentioned here refer to palladium, rhodium, ruthenium, rhenium and platinum. Palladium, rhodium and ruthenium are most preferable. These metals may be used either alone or as an alloy of two or more metals, a so-called bimetal catalyst. The type, shape and size of the carrier are not particularly limited. Activated carbon, alumina and titania are preferable. They may be powders, or molded products such as spheres and pellets. The amount of the noble metal supported on the carrier is between 0.5 and 20% by weight. It is recommendable that the amount supported is between 1 and 20% by weight in powder and between 1 and 10% by weight in molded products. More preferably, a catalyst powder having the amount supported of from 1 to 10% by weight is recommended.

[0041] The reaction pressure is not particularly limited. A pressure in the range of atmospheric pressure to 10 kgf/cm^2 is recommended. The reaction temperature is not particularly limited, either. A temperature in the range of ordinary temperature to 350°C is recommended. Further, the reaction, may be conducted in a liquid phase, or a gaseous phase, as required.

[0042] After the completion of the reaction, as a post-treatment, purification may be conducted by filtering the catalyst, neutralizing and washing the resulting filtrate and conducting distillation. For example, when octafluorocyclopentene (OFCPE) is hydrogenated by the process of this invention, hexafluorocyclopentane can be formed. The boiling point of this compound is between 87 and 88°C at atmospheric pressure, while the boiling point of heptafluorocyclopentane (HFCPA) is 80°C at atmospheric pressure, and the boiling point of octafluorocyclopentane (OFCPA) is 79°C at atmospheric pressure. Accordingly, they can easily be separated through distillation.

[0043] When the fluorinated saturated hydrocarbons (A) and (B) are used in a solvent composition constituting a detergent, the proportion of the fluorinated saturated hydrocarbon (A) having the trihydrofluorocarbon chain usually exceeds 10%, and is preferably 50% by weight or more, more preferably 70% or more, most preferably 80% or more. This is because as the proportion of the trihydrofluorinated saturated hydrocarbon (A) is increased, the non-combustibility of the fluorinated saturated hydrocarbon increase.

[0044] In case of constituting the composition, it is effective to contain at least one organic solvent having a boiling point of at least 25°C and at most 250°C to increase the solubility of contaminants such as oils, flux, waxes and the like. The amount of these organic solvents added is not particularly limited, but is usually 50% by weight or less, preferably between 2 and 30% by weight, more preferably between 3 and 20% by weight based on the total amount. When the organic solvent forms an azeotropic composition, use in the region of the azeotropic composition is preferable.

[0045] The type of such an organic solvent is not particularly limited. For example, at least one organic solvent selected from hydrocarbons, alcohols, esters, chlorinated hydrocarbons, other fluorinated hydrocarbons, ethers, ketones and volatile organic silicones may be used.

[0046] The hydrocarbons mentioned above, are not particularly limited. For example, aliphatic hydrocarbons such as n-pentane, n-hexane, n-heptane, isohexane, isoheptane, n-octane, isooctane, n-decane, isodecane, n-undecane, n-dodecane, n-tridecane and the like, alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane and the like, and aromatic hydrocarbons such as benzene, toluene, xylene and the like can be selected.

[0047] The alcohols mentioned above are not particularly limited either. For example, methanol, ethanol, isopropanol, n-propanol, n-butanol, s-butanol, t-butanol, n-pentanol, isopentanol, n-hexanol, isohexanol, 2-ethylhexanol, n-octanol and the like are mentioned. Of these, those having 5 or less carbon atoms are preferable, and those having 1 to 4 carbon atoms are especially preferable.

[0048] The esters mentioned above are not particularly limited either. For example, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, pentyl acetate, methyl propionate, ethyl propionate, propyl propionate, isopropyl propionate, methyl butyrate, ethyl butyrate, isopropyl butyrate, methyl valerate, ethyl valerate and the like are mentioned. Of these, those having 3 to 10 carbon atoms are preferable, and those having 3 to 6 carbon atoms are especially preferable.

[0049] The chlorinated hydrocarbons mentioned above are not particularly limited. For example, methylene chloride, dichloroethane, dichloroethylene, trichloroethylene, perchloroethylene and the like are mentioned.

[0050] The fluorinated hydrocarbons mentioned above are not particularly limited, and may be mainly

composed of carbon, hydrogen and fluorine and contain oxygen atoms or unsaturated bonds. Of these, those having boiling points of 25°C or more are preferable. As such fluorinated hydrocarbons, for example, pentafluoropropane, hexafluorobutane, decafluoropentane, hexafluorocyclopentane, octafluorocyclopentane, perfluoropropylmethyl ether, perfluorobutylmethyl ether, perfluorobutylethyl ether, hexafluorocyclopentane, heptafluorocyclopentane, octafluorocyclopentene and the like can be used. Further, hexafluorocyclopentane, octafluorocyclopentane, hexafluorocyclopentene and the like having cyclic structures and the appropriate boiling points are preferable.

[0051] The ketones mentioned above are not particularly limited. For example, acetone, 2-butanone, 2-pentanone, 3-pentanone, 2-hexanone, 3-methyl-2-butanone, cyclopentanone, cyclohexanone, 2-methylcyclopentanone, 2-methylcyclohexanone and the like may be selected.

[0052] As the volatile organosilicones mentioned above, hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and the like are mentioned.

[0053] Further, various additives known so far may be added to the detergent of this invention. As additives, there are, for example, stabilizers, surfactants and the like. As the stabilizer, aliphatic nitro compounds such as nitromethane, nitroethane and the like, acetylene alcohols such as 3-methyl-1-butyn-3-ol, 3-methyl-1-pentyn-3-ol and the like, epoxides such as glycidol, methylglycidyl ether, acrylglycidyl ether and the like, ethers such as dimethoxymethane, 1,4-dioxane and the like, unsaturated hydrocarbons such as hexene, heptene, cyclopentene, cyclohexene and the like, unsaturated alcohols such as allyl alcohol, 1-buten-3-ol and the like, acrylates such as methyl acrylate, ethyl acrylate and the like, and so forth are mentioned.

[0054] Further, as the surfactant, anionic surfactants, cationic surfactants, nonionic surfactants, and amphoteric surfactants known so far maybe used. As the anionic surfactant, for example, a carboxylate, a sulfonate, a sulfate, a phosphate and the like may be used. As the cationic surfactant, for example, salts of amines and various acids and quaternary ammonium salts are mentioned. As the nonionic surfactant, for example, polyoxyethylene ether, polyoxyethylene-polyoxypropylene glycol, polyoxyethylene-polyoxypropylene alkyl ether, polyhydric alcohol aliphatic acid partial ester and the like are mentioned. As the amphoteric surfactant, for example, betaines, organic amino acids, amine salts of fatty acids and the like are mentioned. Further, surfactants containing fluorine atoms are also preferable. When these surfactants are added, it is possible to effectively remove and dry the water adhered to processed parts of metals, ceramics, glasses, plastics, elastomers and the like, after water-washing. The amount of the surfactant is not particularly limited. It is usually 30% by weight or less, preferably 20% by weight or less, more preferably between 0.005 and 10% by weight based on the total amount.

[0055] The products to be washed are not particularly limited either. For example, metals, ceramics, glasses, plastics, elastomers and the like used in industries such as the precision machinery industry, the metal processing industry, the optical machinery industry, the electronic industry, and plastics industry may be washed with the product of this invention. Specifically, a wide variety of products such as automobile parts, as in bumpers, gears, mission parts, and radiator parts, electronic and electric parts such as printed circuit boards, IC parts, lead frames, motor parts, and condensers, precision machine parts such as bearings, gears, engineering plastics gears, watch parts, camera parts, optical lenses and such, large-sized machine parts such as printers, printer blades, printing rolls, flat rolled products, building machines, glass substrates, and large-sized heavy machine parts, household products such as tableware, and fiber products may be mentioned as examples.

[0056] The types of the contaminants, removed by product of the present invention, may be oils such as cutting oils, quenching oils, rolling oils, lubricants, machine oils, press oils, blanking oils, drawing oils, assembling oils, and wire drawing oils, as well as greases, waxes, adhesives, fats and oils, release agents in molding, thumb-marks, flux after soldering, resists, and solder pastes.

[0057] With respect to the washing method, the product to be washed may be washed by its contact with the washing solvent composition, using regular washing methods. Specifically, methods such as hand wiping, dipping, spraying, showering or the like may be applied. In these treatments, physical means such as ultrasonic vibration, shaking, stirring, brushing or the like may be used in combination.

[0058] In the washing process, an organic solvent made of at least one type selected from aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons, alcohols, esters, chlorinated hydrocarbons, ethers, ketones and volatile organosilicones may also be used as a solvent other than the detergent of the present invention.

[0059] In such a case, a method comprising two steps, a step of removing contaminants of the product to be washed and a step of rinsing an organic solvent adhered to the product after the removal of contaminants by contacting the same with the detergent of this invention or vapor-cleaning the same in a vapor of a detergent (so-called co-solvent system), is employed.

[0060] On the basis of the foregoing, preferred modes for carrying out this invention are summed up below.

1. The trihydrofluorinated saturated hydrocarbon (A) is a cyclic fluorinated saturated hydrocarbon.
2. The number of carbon atoms in trihydrofluori-

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nated saturated hydrocarbon is between 3 and 10.

3. The number of carbon atoms in the above-mentioned 2 is between 4 and 6.

4. The number of carbon atoms in the above-mentioned 3 is 5.

5. The trihydrofluorinated saturated hydrocarbon in the above-mentioned 4 is cyclic.

6. The trihydrofluorinated saturated hydrocarbon is 1,1,1,2,2,3,5,5,5-nonafluoro-n-pentane, 1,1,1,2,2,4,5,5,5-nonafluoro-n-pentane or 1,1,2,2,3,3,4-heptafluorocyclopentane.

7. The fluorinated saturated hydrocarbon of formula (III) is selectively produced through catalytic reduction by making the component other than the substrate starting material of the reaction system to have a high polarity.

8. In the above-mentioned 7, the catalytic reduction is conducted using a starting material in which the proportion of the high-polarity compound in the impurities is increased by adding a high-polarity compound in the fluorinated unsaturated hydrocarbon represented by formula (V) used as the substrate starting material, or by removing the low-polarity compound from the impurities accompanying the substrate starting material.

9. The fluorinated saturated hydrocarbon of formula (IV) is selectively produced through catalytic reduction by making the component other than the substrate starting material of the reaction system have a low polarity.

10. In the above-mentioned 9, the catalytic reduction is conducted using a starting material in which the proportion of the low-polarity compound in the impurities is increased by adding a low-polarity compound in the fluorinated unsaturated hydrocarbon represented by formula (V) used as the substrate starting material, or by removing the high-polarity compound from the impurities in the substrate starting material.

11. In the above-mentioned 8, the low-polarity compound is added to the starting material in an amount of 0.5% by weight or less.

12. In the above-mentioned 8, the high-polarity compound is contained in the starting material in an amount of 0.1 to 15% by weight.

13. In the above-mentioned 10, the high-polarity compound is added to the starting material in an amount of 0.5% by weight.

14. In the above-mentioned 10, the low-polarity compound is added to the starting material in an amount of 0.1 to 15% by weight.

15. In the above-mentioned 8 or 10, the low-polarity compound is a paraffin, naphthene or aromatic compound.

16. In the above-mentioned 8 or 10, the high-polarity compound is an alcohol, a polyhydric alcohol, a polyhydric alcohol monoether, an amide, or a sulfoxide.

17. In the above-mentioned 8, the low-polarity compound accompanying the substrate starting material reduces the content in the starting material by adsorption treatment with an adsorbent.

18. In the above-mentioned 10, the high-polarity compound accompanying the substrate starting material reduces the content in the starting material by adsorption treatment with an adsorbent.

19. In the above-mentioned 7, a trihydrofluorinated saturated hydrocarbon of formula (III) is selectively produced by using a fluorinated unsaturated hydrocarbon having carbon chains of -CF=CF- as in formula (V) as the starting material, in which the symbol X represents a fluorine atom.

20. In the above-mentioned 9, a trihydrofluorinated saturated hydrocarbon of formula (IV) is selectively produced by using a fluorinated, unsaturated hydrocarbon having a carbon chain of -CH=CF- as in formula (V) as the starting material, in which the symbol X represents a hydrogen atom.

21. The fluorinated, unsaturated hydrocarbon of formula (V) as the starting material in the above-mentioned 7 or 9 has 3 to 10 carbon atoms.

22. The number of carbon atoms in the above-mentioned 21 is between 4 and 6.

23. The fluorinated, unsaturated hydrocarbon used as the starting material in the above-mentioned 19 is 1,1,1,2,3,3-hexafluoropentene, 1,1,1,2,2,3,4,5,5,5-decafluoro-n-pentene or 1,1,2,2,3,3,4,5-octafluorocyclopentene.

24. The fluorinated, unsaturated hydrocarbon used as the starting material in the above-mentioned 20 is 1,1,1,2,3-pentafluoropropene, 1,1,1,3,3-pentafluoropropene, 1,1,1,2,2,3,5,5,5-nonafluoro-n-pentene or 1,1,2,2,3,3,4-heptafluorocyclopentene.

25. In the above-mentioned 7 or 9, the catalytic reduction is conducted under hydrogen in the presence of a noble metal catalyst.

26. In the above-mentioned 25, the noble metal is palladium, rhodium, ruthenium, rhenium or platinum.

27. In the above-mentioned 26, the noble metal is palladium, rhodium or ruthenium.

28. In the above-mentioned 25, the noble metal catalyst is one in which the noble metal is contained in a carrier.

29. In the above-mentioned 28, the carrier is activated carbon, alumina or titania.

30. In the above-mentioned 28, the amount of metal contained in the carrier is between 0.5 and 20% by weight.

31. In the above-mentioned 25, the catalytic reduction is conducted as a liquid phase reaction or a gaseous phase reaction at a pressure in the range of atmospheric pressure to 10 kg/cm^2, in a hydrogen atmoshpere, and a temperature in the range of ordinary temperature to 350°C.

32. In a composition containing the fluorinated sat-

urated hydrocarbons (A) and (B), the proportion of the trihydrofluorinated saturated hydrocarbon (A) exceeds 10 mol%.

33. In the above-mentioned 32, it is 50 mol% or more.

34. In the above-mentioned 33, it is 70 mol% or more.

35. In the above-mentioned 34, it is 80 mol% or more.

36. In the above-mentioned 32, an organic solvent having a boiling point of at least 25°C and at most 250°C, is 50% or less by weight of the total amount.

37. In the above-mentioned 36, it is between 2 and 30% by weight.

38. In the above-mentioned 37, it is between 3 and 20% by weight.

39. In the above-mentioned 36, the organic solvent is a hydrocarbon, an alcohol, an ester, a chlorinated hydrocarbon, a fluorinated hydrocarbon, an ether, a ketone or a volatile organosilicone.

[0061] The mode for carrying out this invention is illustrated more specifically by referring to the following Examples.

Example 1:

[0062] One percent by weight of n-tridecane (dielectric constant 2.0), a low-polarity compound, was dissolved in crude 1,3,3,4,4,5,5-heptafluorocyclopentene having a purity of 99.9 GC%. An autoclave having a capacity of 100 ml was charged with a catalyst of activated carbon having supported thereon 5% by weight of powdered palladium. After the deaeration under reduced pressure, n-tridecane-containing 1,3,3,4,4,5,5-heptafluorocyclopentene prepared previously was poured. While the mixture was stirred at 40°C, the reaction was conducted by repeating block charge of hydrogen at a gauge pressure in the range of 0 to 6 kgf/cm^2. After the completion of the reaction, the product was analyzed through gas chromatography. Consequently, a fluorinated saturated hydrocarbon containing 94 mol% of 1,1,2,2,3,3,4-heptafluorocyclopentane (HFCPA) and 6 mol% of 1,1,2,2,3,3-hexafluorocyclopentane was obtained.

Example 2:

[0063] The reaction was conducted as in the above-mentioned Example 1 without adding n-tridecane. Consequently, a product containing 70 mol% of 1,1,2,2,3,3,4-heptafluorocyclopentane and 30 mol% of 1,1,2,2,3,3-hexafluorocyclopentane was obtained.

Example 3:

[0064] Activated carbon as a typical nonionic adsorbent was charged into crude octafluorocyclopentene containing low-polarity hydrocarbon impurities and having a purity of 99 GC%. These were stirred, and filtered to remove the low-polarity compound from the impurities of the crude starting material. Octafluorocyclopentene having a purity of 99.9 GC% in which the proportion of the high-polarity compound in the impurity was increased was obtained. Then, an autoclave having a capacity of 100 ml was charged with a catalyst of activated carbon having supported thereon 5% by weight of palladium powder. After the deaeration under reduced pressure, octafluorocyclopentene (dielectric constant: 2.6) having a purity of 99.9% as prepared previously was poured in. While the mixture was stirred at 40°C, the reaction was conducted by repeating block charge of hydrogen at a gauge pressure in the range of 0 to 6 kgf/cm^2. After the completion of the reaction, the product was analyzed through gas chromatography. Consequently, a fluorinated saturated hydrocarbon containing 75 mol% of heptafluorocyclopentane (HFCPA) and 25 mol% of octafluorocyclopentane (OFCPA) was obtained.

Example 4:

[0065] Crude octafluorocyclopentene having a purity of 99 GC% was mixed with the same volume of diethylene glycol monomethyl ether as a high-polarity compound. An autoclave having a capacity of 100 ml was charged with a catalyst of activated carbon having supported thereon 5% by weight of palladium powder. After the deaeration under reduced pressure, the mixture of octafluorocyclopentene and diethylene glycol monomethyl ether prepared previously was poured. While the resulting mixture was stirred at 40°C, the reaction was conducted by repeating block charge of hydrogen at a gauge pressure in the range of 0 to 6 kgf/cm^2. After the completion of the reaction, the product was analyzed through gas chromatography. Consequently, a fluorinated saturated hydrocarbon containing 85 mol% of heptafluorocyclopentane (HFCPA) and 15 mol% of octafluorocyclopentane (OFCPA) was obtained.

Example 5:

[0066] Crude hexafluoropropene containing low-polarity hydrocarbon impurity and having a purity of 98 GC% was previously subjected to adsorption treatment with activated carbon as in Example 3 to remove the low-polarity compound from the impurities of the crude starting material. The product having a purity of 99.2 GC% in which the proportion of the high-polarity compound in the impurities was increased, was subjected to a hydrogenation reaction. Consequently, fluorinated propane comprising 72 mol% of trihydrofluoropentapropane composed of 1,1,1,2,3-pentafluoropropane and 1,1,1,3,3-pentafluoropropane and 28 mol% of 1,2-dihydrohexafluoropropane was obtained.

Example 6:

[0067] Decafluoro-2-pentene in which the content of the low-polarity hydrocarbon impurity was controlled to 0.4% by weight from the product having a purity of 98 GC% was subjected to a hydrogenation reaction in the presence of diethylene glycol monomethyl ether as in Example 4.

[0068] Fluorinated pentane comprising 73 mol% of trihydrononafluoropentane composed of 1,1,1,2,2,3,5,5,5-nonafluoropentane and 1,1,1,2,2,4,5,5,5-nonafluoropentane and 27 mol% of 2,3-dihydrodecafluoropentane was obtained.

Example 7:

[0069] One percent by weight of n-tridecane (dielectric constant 2.0), a low-polarity compound, was dissolved in crude octafluorocyclopentene having a purity of 99.9 GC%. An autoclave having a capacity of 100 ml was charged with a catalyst of activated carbon containing 5% by weight of palladium powder. After deaeration under reduced pressure, n-tridecane-containing octafluorocyclopentene prepared previously was poured in. While the mixture was stirred at 40°C, the reaction was conducted by repeating the block charge of hydrogen at a gauge pressure in the range of 0 to 6 kgf/cm^2. The product obtained was analyzed through gas chromatography. Consequently, a fluorinated saturated hydrocarbon containing 83 mol% of octafluorocyclopentane (OFCPA) and 17 mol% of heptafluorocyclopentane (HFCPA) was obtained.

Example 8:

[0070] n-Tridecane (3% by weight), a low-polarity compound was dissolved in crude octafluorocyclopentene having a purity of 99.9 GC%. An autoclave having a capacity of 100 ml was charged with a catalyst of activated carbon having supported thereon 5% by weight of palladium powder. After the deaeration under reduced pressure, n-tridecane-containing octafluorocyclopentene prepared previously was poured in. While the mixture was stirred at 40°C, the reaction was conducted by repeating block charge of hydrogen at a gauge pressure in the range of 0 to 6 kgf/cm^2. After the completion of the reaction, the product was analyzed through gas chromatography. Consequently, a fluorinated saturated hydrocarbon containing 86 mol% of octafluorocyclopentane (OFCPA) and 14 mol% of heptafluorocyclopentane (HFCPA) was obtained.

Example 9:

[0071] One percent by weight of o-xylene (dielectric constant 2.6), a low-polarity compound was dissolved in crude octafluorocyclopentene having a purity of 99.9 GC%. An autoclave having a capacity of 100 ml was charged with a catalyst of activated carbon having containing 5% by weight of palladium powder. After the deaeration under reduced pressure, o-xylene-containing octafluorocyclopentene prepared previously was poured. While the mixture was stirred at 40°C, the reaction was conducted by repeating block charge of hydrogen at a gauge pressure in the range of 0 to 6 kgf/cm^2. After the completion of the reaction, the product was analyzed through gas chromatography. Consequently, a fluorinated saturated hydrocarbon containing 87 mol% of octafluorocyclopentane (OFCPA) and 13 mol% of heptafluorocyclopentane (HFCPA) was obtained.

Example 10:

[0072] Activated alumina as a typical ionic adsorbent was charged into crude octafluorocyclopentene having a purity of 99 GC%. These were stirred, and filtered to remove the high-polarity impurity from the impurities of the crude starting material. Octafluorocyclopentene having a purity of 99.5 GC% in which the proportion of the low-polarity compound, in the impurities was increased, was obtained. An autoclave having a capacity of 100 ml was charged with a catalyst of activated carbon having supported thereon 5% by weight of palladium as a powder. After the deaeration under reduced pressure, octafluorocyclopentene having a purity of 99.5% as obtained previously was poured. While the mixture was stirred at 40°C, the reaction was conducted by repeating block charge of hydrogen at a gauge pressure in the range of 0 to 6 kgf/cm^2. After the completion of the reaction, the product was analyzed through gas chromatography. Consequently, a fluorinated saturated hydrocarbon containing 74 mol% of octafluorocyclopentane (OFCPA) and 26 mol% of heptafluorocyclopentane (HFCPA) was obtained.

Example 11:

[0073] A flux (PO-F-1010S made by Senju Metal Industry Co., Ltd.) was coated on the whole surface of a printed substrate (30 mm x 30 mm x 0.2 mm in thickness) made of a polyimide resin, and dried at room temperature. This was dipped in a detergent composition of 80 parts by weight of a fluorinated saturated hydrocarbon of heptafluorocyclopentane: hexafluorocyclopentane = 0:40 (molar ratio) and 20 parts by weight of ethanol at 30°C for 3 minutes. The condition of removing the flux was visually observed. Consequently, it was identified that the flux was completely removed.

Example 12:

[0074] A product obtained by aligning 50 press-molded parts (made of stainless steel, 50 mm square) and bundling the same with a wire was prepared. This was dipped in a beaker containing a press oil (Tafuny Punch Oil made by Idemitsu Kosan Co., Ltd.) at room

temperature, and an ultrasonic wave was applied for 1 minute to coat the press oil throughout the product. The product was allowed to stand as such in the solution for 30 minutes, and was then withdrawn from the press oil. The product was allowed to stand for 5 minutes for removal of the oil. This sample was dipped in a fluorinated saturated hydrocarbon of heptafluorocyclopentane: hexafluorocyclopentane = 80:20 (molar ratio) at 50°C for 3 minutes while applying an ultrasonic wave, and further steam-washed in the steam of the same fluorinated saturated hydrocarbon as mentioned above. After cooling, the removal of the oil was visually observed, and the odor was confirmed. Consequently, it was identified that the oil was completely removed.

Example 13:

[0075] A test for drying by draining was conducted using the same fluorinated saturated hydrocarbon as in Example 1.

[0076] A cover glass (15 mm x 15 mm) was previously washed by degreasing. This was dipped as a test piece in pure water, and then in 100 ml of the composition in Example 1 for 30 seconds. The test piece was withdrawn, and allowed to stand at room temperature for 1 minute for the evaporation of the residual composition.

[0077] Subsequently, it was placed in 10 g of ethanol (water content 570 ppm), and the water content increased of ethanol was measured with a Karl Fischer's water content meter. Consequently, it was 30 ppm.

[0078] The increase in water content for a blank was measured using a cover glass which was allowed to stand at room temperature. Consequently, it was 50 ppm.

[0079] Further, the increase in water content of a product which was dipped in pure water alone and not in the composition was 3,200 ppm.

[0080] In view of the foregoing, it was found that drying by draining could be conducted almost completely by using the composition of this Example.

Industrial Applicability:

[0081] The invention of this application has made it possible, for the first time, to provide a hydrofluorocarbon (HFC), which have been known to cause no damage in the ozone layter, and to have a small global heating coefficient, especially a fluorinated saturated hydrocarbon containing high proportions of trihydrofluorocarbon, which is excellent in its chemical stability and its safety towards animals. Consequently, a fluorinated saturated hydrocarbon containing, in a high proportion, trihydrofluorocarbon which can safely be used as a substitute compound of CFC (chlorofluorocarbon) or HCFC (hydrochlorofluorocarbon) that has found so far wide acceptance as detergents, drain-drying agents, foaming agents, refrigerants and the like, can widely be supplied on the market.

[0082] And it goes without saying that the fluorinated hydrocarbon of the invention of this application can be used as a detergent, a rinse detergent, a vapor-cleaning detergent, a gap detergent or a drain-drying detergent.

[0083] Further, with respect to the other specific use, there are, for example, various test solvents such as solvents for testing the voltage resistance of a switch, solvents for testing ceramics polarization, solvents for testing the voltage resistance of a cathode ray tube socket, solvent for testing the voltage resistance of a film condenser and the like; liquid mediums for rectifiers; liquid mediums for transformers; liquid mediums for condensers; cooling • heating liquid mediums for cooling in semiconductor production or cooling of a dry etching device, cooling of ozone devices, cooling of liquid crystal projectors, cooling of power supply heat exchangers or the like; solvents for the production of a fluoropolymers; solvents for film formation with a fluorine/silicone polymer; detergents for hollow fibers; dry cleaning solvents; solvent of a fluorine-containing electrolytes; solvents for forming surface lubricant layer of magnetic disks or magnetic tapes; solvent for checking cracks or leak of castings, ceramics product or the like; chemical reaction solvents in a reaction using a Lewis acid catalyst or the like; blow washing solvents; solvents for polishing disks such as a silicon wafer substrate, metallic substrate, glass substrate or the like; detergents for production of conductor IC chips; solvent for surface treatment of a printed circuit board; solvent for chemical mechanical polishing; photoresist solvents; developer solvents; rinse compositions; and so forth. It can also be used as medical mediums. For example, there are aerosol solvents for human bodies containing agents such as anti-inflammatory agents, muscular fatigue treating agents, local warming agents, analgesic or antipruritic agents, blood circulation accelerators, external agents of formulation for coating or spraying onto the human skin, inhalants, collunariums, deodorants, disinfectants, clean wiping agents or the like; mediums for air sterilization; detergents for the sterilization of dialysis hollow fibers; mediums for cryoperation using a catheters or cooling a medical cooler of the head or the like; polymer-containing liquids for forming polymer films on surfaces of disposal products such as catheters, insert units, guide wires, circuits, sensors and the like, and embedding products such as artificial blood vessels, stents, an artificial bones and the like; detergents of disposal products such as catheters, insert units, guide wires, injection needles, circuits, bags, sensors and the like, embedding products such as artificial blood vessels, stents, artificial bones, dental members and the like, and rigid units such as forcepses, cutters (scissors), tweezers, rib spreaders and the like; pressure mediums for continuously administering small amounts of drugs to the affected portions; solvents for production of drug-containing gelatin capsules; solvents for coating a lubricants and solvents for removing a

lubricants in production of medical catheters; solvents for coating lubricants and solvents for removing lubricants in artificial organs, artificial blood vessels and the like; and so forth.

Claims

1. A fluorinated saturated hydrocarbon which is an acyclic or cyclic fluorinated saturated hydrocarbon characterized by comprising less than 95 mol% of a trihydrofluorinated saturated hydrocarbon (A) represented by the following formula (I)

$$Rf_1\text{-}R_1\text{-}Rf_2 \quad (I)$$

(wherein R_1 represents a carbon chain in which CHF and CH_2 are bound, Rf_1 and Rf_2 each represents a perfluoroalkyl group, a fluorine atom or a hydrogen atom, at least one thereof is a perfluoroalkyl group, and further Rf_1 and Rf_2 may be bound to each other to form a ring by a perfluoroalkylene chain)

and the balance of a tetrahydrofluorinated saturated hydrocarbon (B) having the same carbon number and the same carbon structure as said trihydrofluorinated saturated hydrocarbon (A), as represented by the following formula (II)

$$Rf_1\text{-}R_2\text{-}Rf_2 \quad (II)$$

(wherein R_2 represents a carbon chain in which CH_2 and CH_2 are bound, and Rf_1 and Rf_2 are as defined above).

2. The fluorinated saturated hydrocarbon of claim 1, wherein the trihydrofluorinated saturated hydrocarbon (A) is an alicyclic, fluorinated hydrocarbon having 4 to 6 carbon atoms.

3. The fluorinated saturated hydrocarbon of claim 1, wherein the boiling point of the fluorinated saturated hydrocarbon is at least 25°C and at most 150°C.

4. The fluorinated saturated hydrocarbon of claim 1, wherein the proportion of the trihydrofluorinated saturated hydrocarbon (A) is 10 mol% or more.

5. The fluorinated saturated hydrocarbon of claim 1, wherein the proportion of the trihydrofluorinated saturated hydrocarbon (A) is 50 mol% or more.

6. A process for producing a fluorinated saturated hydrocarbon comprising a compound represented by the following formula (III)

$$Rf_1\text{-}R_1\text{-}Rf_2 \quad (III)$$

(wherein R_1 represents a carbon chain in which CHX and CH_2 are bound, X represents a hydrogen atom or a fluorine atom, Rf_1 and Rf_2 each represent a perfluoroalkyl group, a fluorine atom or a hydrogen atom, at least one thereof is a perfluoroalkyl group, and further Rf_1 and Rf_2 may be bound to each other to form a ring by a perfluoroalkylene chain)

and a compound represented by the following formula (IV)

$$Rf_1\text{-}R_2\text{-}Rf_2 \quad (IV)$$

(wherein R_2 represents a carbon chain in which CHX and CHF are bound, and X, Rf_1 and Rf_2 are as defined above),

characterized in that when a fluorinated, unsaturated hydrocarbon represented by the following formula (V)

$$Rf_1\text{-}R_3\text{-}Rf_2 \quad (V)$$

(wherein R_3 represents a carbon chain of -CX=CF-, X represents a hydrogen atom or a fluorine atom, Rf_1 and Rf_2 each represent a perfluoroalkyl group, a fluorine atom or a hydrogen atom, at least one thereof is a perfluoroalkyl group, and further Rf_1 and Rf_2 may be bound to each other to form a ring by a perfluoroalkylene chain)

is catalytically reduced under hydrogen using a novel metal catalyst, the proportions of the fluorinated saturated hydrocarbon of formula (III) and the fluorinated saturated hydrocarbon of formula (IV) are controlled by changing the polarity of the component other than the substrate starting material of the reaction system.

7. The process for producing the fluorinated saturated hydrocarbon of claim 6, wherein the fluorinated saturated hydrocarbon of formula (III) is selectively produced through catalytic reduction by making the component other than the substrate starting material of the reaction system to have a high polarity.

8. The process for producing the fluorinated saturated hydrocarbon of claim 7, wherein the catalytic reduction is conducted using a starting material in which the proportion of the high-polarity compound in impurities is increased by containing the high-polarity compound in the fluorinated, unsaturated hydrocarbon represented by formula (V) as the substrate starting material or by removing a low-polarity compound from among impurities accompanying the substrate starting material.

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9. The process for producing the fluorinated saturated hydrocarbon of claim 6, wherein the fluorinated saturated hydrocarbon of formula (IV) is selectively produced through catalytic reduction by making the component other than the substrate starting material of the reaction system to have a low polarity.

10. The process for producing the fluorinated saturated hydrocarbon of claim 9, wherein the catalytic reduction is conducted using a starting material in which the proportion of the low-polarity compound in impurities is increased by containing the low-polarity compound in the fluorinated, unsaturated hydrocarbon represented by formula (V) as the substrate starting material or by removing the high-polarity compound from among impurities accompanying the substrate starting material.

11. The process for producing the fluorinated saturated hydrocarbon of claim 8, wherein the low-polarity compound is contained in the starting material in an amount of 0.5% by weight or less, or the high-polarity compound is contained in the starting material in an amount in the range of 0.1 to 15% by weight.

12. The process for producing the fluorinated saturated hydrocarbon of claim 10, wherein the high-polarity compound is contained in the starting material in an amount of 0.5% by weight or less, or the low-polarity compound is contained in the starting material in an amount in the range of 0.1 to 15% by weight.

13. The process for producing the fluorinated saturated hydrocarbon of claim 8 or 10, wherein the low-polarity compound is paraffins, naphthenes or aromatics, and the high-polarity compound is alcohols, polyhydric alcohols, polyhydric alcohol monoethers, amides or sulfoxides.

14. The process for producing the fluorinated saturated hydrocarbon of claim 7, wherein a trihydrofluorinated saturated hydrocarbon of formula (III) is selectively produced by using a fluorinated, unsaturated hydrocarbon having a carbon chain of -CF=CF- in which the symbol in formula (V) represents a fluorine atom as a starting material.

15. The process for producing the fluorinated saturated hydrocarbon of claim 9, wherein a trihydrofluorinated saturated hydrocarbon of formula (IV) is selectively produced by using a fluorinated, unsaturated hydrocarbon having a carbon chain of -CH=CF- in which the symbol in formula (V) represents a fluorine atom as a starting material.

16. The process for producing the fluorinated saturated hydrocarbon of claim 7 or 9, wherein formula (V) of the starting material is an alicyclic fluorinated, unsaturated hydrocarbon having 4 to 6 carbon atoms.

17. The process for producing the fluorinated saturated hydrocarbon of claim 6, wherein the noble metal is palladium, rhodium, ruthenium, rhenium or platinum.

18. The process for producing the fluorinated saturated hydrocarbon of claim 6, wherein the catalytic reduction is conducted as a liquid phase reaction or a gaseous phase reaction at a temperature in the range of ordinary temperature to 350°C under hydrogen of a pressure in the range of atmospheric pressure to 10 kg/cm^2.

19. A composition of a fluorinated saturated hydrocarbon which is a composition of the fluorinated saturated hydrocarbon of any one of claims 1 to 5, characterized in that at least one type of an organic solvent having a boiling point of at least 25°C and at most 250°C is contained along with the fluorinated saturated hydrocarbon compounds.

20. The composition of the fluorinated saturated hydrocarbon of claim 19, wherein the organic solvent having the boiling point of at least 25°C and at most 250°C is 50% by weight or less based on the total amount.

21. The composition of the fluorinated saturated hydrocarbon of claim 20, wherein the organic solvent is between 2 and 30% by weight based on the total amount.

22. The composition of the fluorinated saturated hydrocarbon of claim 20, wherein the organic solvent is hydrocarbons, alcohols, esters, chlorinated hydrocarbons, fluorinated hydrocarbons, ethers, ketones or volatile organosilicones.

INTERNATIONAL SEARCH REPORT

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PCT/JP98/02157

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[6] C07C19/08, 23/02, C10M107/38, 147/02, C11D7/50, C09K3/00, C09K5/04

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B. FIELDS SEARCHED

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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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 5-302098, A (Asahi Glass Co., Ltd.), 16 November, 1993 (16. 11. 93) (Family: none)	1-5, 19-22
X	JP, 5-508418, A (E.I. Du Pont de Nemours & Co.), 25 November, 1993 (25. 11. 93) & WO, 92/06941, A1 & EP, 552252, A1 & US, 5171902, A & US, 5504256, A & US, 5683978, A & US, 5723701, A	1-22
Y	JP, 4-25598, A (Nippon Zeon Co., Ltd.), 29 January, 1992 (29. 01. 92) & EP, 458279, A1	1-5, 19-22
Y	JP, 6-41589, A (Asahi Glass Co., Ltd.), 15 February, 1994 (15. 02. 94) (Family: none)	1-5, 19-22
Y	JP, 5-331490, A (Asahi Glass Co., Ltd.), 14 December, 1993 (14. 12. 93) (Family: none)	1-5, 19-22
A	JP, 5-331489, A (Asahi Glass Co., Ltd.), 14 December, 1993 (14. 12. 93) (Family: none)	1-5, 19-22

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(71) Applicant *(for all designated States except US)*: **E.I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **NAPPA, Mario, Joseph** [US/US]; 3 Oakridge Court, Newark, Delaware 19711 (US).

(74) Agent: **HAMBY, Jane, O.**; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

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(54) Title: COPRODUCTION OF HYDROFLUOROOLEFINS

(57) Abstract: Disclosed is a process for the co-manufacture of the hydrofluoroolefins HFC-1225ye and HFC-1234yf. The process comprises contacting a blend of 1,1 ,1, 2,3,3-hexafluoropropane and 1,1,1,2,3- pentafluoropropane at a temperature of from about 200 °C to about 500 °C with a catalyst, optionally in the presence of an inert gas. The catalyst includes, but is not limited to, aluminum fluoride; fluorided alumina; metals on aluminum fluoride; metals on fluorided alumina; oxides, fluorides, and oxyfluorides of magnesium, zinc and mixtures of magnesium and zinc and/or aluminum; lanthanum oxide and fluorided lanthanum oxide; chromium oxides, fluorided chromium oxides, and cubic chromium trifluoride; carbon, acid-washed carbon, activated carbon, three dimensional matrix carbonaceous materials; and metal compounds supported on carbon. The metal compounds are oxides, fluorides, and oxyfluorides of at least one metal selected from the group consisting of sodium, potassium, rubidium, cesium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, chromium, iron, cobalt, rhodium, nickel, copper, zinc, and mixtures thereof. The product hydrofluoroolefins are separated from unreacted hydrofluorocarbons and hydrogen fluoride. In another embodiment, the unreacted hydrofluorocarbons optionally may be recirculated back through the process.

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TITLE OF THE INVENTION

COPRODUCTION OF HYDROFLUOROOLEFINS

BACKGROUND OF THE INVENTION

Field of the Invention.

[0001] The present disclosure relates to the field of production and purification of hydrofluoroolefin compounds. This invention particularly relates to a method for the co-manufacture of 1,2,3,3,3-pentafluoropropene (FC-1225ye) and 2,3,3,3-tetrafluoropropene (FC-1234yf) via the catalytic dehydrofluorination of 1,1,1,2,3,3-hexafluoropropane and 1,1,1,2,3-pentafluoropropane.

Description of Related Art.

[0002] Chlorine-containing compounds such as chlorofluorocarbons (CFCs) are considered to be detrimental to the Earth's ozone layer. Many of the hydrofluorocarbons (HFCs), used to replace CFCs, have been found to contribute to global warming. Therefore, there is a need to identify new compounds that do not damage the environment, but also possess the properties necessary to function as refrigerants, solvents, cleaning agents, foam blowing agents, aerosol propellants, heat transfer media, dielectrics, fire extinguishing agents, sterilants and power cycle working fluids. Fluorinated olefins, especially those containing one or more hydrogens in the molecule (referred to herein as hydrofluoroolefins) are being considered for use in some of these applications such as in refrigeration as well as in processes to make fluoropolymers. Blends of HFC-1225ye and HFC-1234yf are useful as refrigerant compositions which have lower potential to contribute to global warming than refrigerant compositions such as blends of HFC-134a. Particularly useful are blends for HFC-1225ye and HFC-1234yf which contain greater than 50% by weight of HFC-1225ye, which renders the blend nonflamable

[0003] U.S. Patent 6369284 describes a method for making HFC 1225ye or HFC 1225zc from HFC-236ea or HFC-236fa respectively by dehydrofluorination. U.S. Patent 6548719 describes a method of

dehydrohalogenating hydrofluorocarbons to produce hydrofluoroolefins such as HFC-1234ze using alkali metal hydroxides with phase tranfer catalysts. U.S. Patents 5679875 and 5396000 disclose a method for making HFC-1225ye from HFC-236ea via catalytic dehydrofluorination. Pending U.S. application 11/264,183 discloses dehydrofluorination of hydrofluorocarbons to produce hydrofluoroolefins.

[0004] Blends of HFC-1225ye and HFC-1234yf are particularly useful as refrigerant compositions which have lower global warming potential than hydrofluorocarbons currently in use. It would be useful from a manufacturing perspective to be able to directly manufacture a desired blend in a single process instead of having to blend the two HFC's produced invidually.

BRIEF SUMMARY OF THE INVENTION

[0005] In one embodiment, a process is provided for the co-manufacture of hydrofluoroolefins HFC-1225ye and HFC-1234yf. The process comprises contacting a blend of 1,1,1,2,3,3-hexafluoropropane and 1,1,1,2,3-pentafluoropropane at a temperature of from about 200 °C to about 500 °C with a catalyst, optionally in the presence of an inert gas. The catalyst includes, but is not limited to, aluminum fluoride; fluorided alumina; metals on aluminum fluoride; metals on fluorided alumina; oxides, fluorides, and oxyfluorides of magnesium, zinc and mixtures of magnesium and zinc and/or aluminum; lanthanum oxide and fluorided lanthanum oxide; chromium oxides, fluorided chromium oxides, and cubic chromium trifluoride; carbon, acid-washed carbon, activated carbon, three dimensional matrix carbonaceous materials; and metal compounds supported on carbon. The metal compounds are oxides, fluorides, and oxyfluorides of at least one metal selected from the group consisting of sodium, potassium, rubidium, cesium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, chromium, iron, cobalt, rhodium, nickel, copper, zinc, and mixtures thereof. The product hydrofluoroolefins are separated from unreacted hydrofluorocarbons and hydrogen fluoride.

In another embodiment, the unreacted hydrofluorocarbons optionally may be reciculated back through the process.

DETAILED DESCRIPTION OF THE INVENTION

[0006] This invention provides a process for the production of a blend of *cis*- and *trans*-1,2,3,3,3-pentafluoropropene (*i.e.*, $CF_3CF=CHF$ or HFC-1225ye)(hereinafter referred to a simply as 1,2,3,3,3-pentafluoropropene, or HFC-1225ye) and 2,3,3,3-tetrafluoropropene (*i.e.*, $CF_3CF=CH_2$ or HFC-1234yf) from 1,1,1,2,3,3-hexafluoropropane (*i.e.*, $CF_3CHFCHF_2$ or HFC-236ea) and 1,1,1,2,3-pentafluoropropane (*i.e.*, CF_3CHFCH_2F or HFC-245eb). HFC-236ea and HFC-245eb can be readily prepared by known art methods. HFC-236cb for example can be readily prepared by hydrogenation of hexafluoropropene in the presence of a Pd/C catalyst.

[0007] In accordance with one embodiment of the invention, a blend of HFC-236ea and HFC-245eb is dehydrofluorinated, thereby forming a product mixture of HFC-1225ye and HFC-1234yf over a selected catalyst.

[0008] The dehydrofluorination of a hydrofluorocarbon may be carried out in the vapor phase. Vapor phase dehydrofluorination of a hydrofluorocarbon may be suitably carried out using typical dehydrofluorination catalysts. Generally, the present dehydrofluorination may be carried out using any dehydrofluorination catalyst known in the art. These catalysts include, but are not limited to, aluminum fluoride; fluorided alumina; metals on aluminum fluoride; metals on fluorided alumina; oxides, fluorides, and oxyfluorides of magnesium, zinc and mixtures of magnesium and zinc and/or aluminum; lanthanum oxide and fluorided lanthanum oxide; chromium oxides, fluorided chromium oxides, and cubic chromium trifluoride; carbon, acid-washed carbon, activated carbon, three dimensional matrix carbonaceous materials; and metal compounds supported on carbon. The metal compounds are oxides, fluorides, and oxyfluorides of at least one metal selected from the group consisting of sodium, potassium, rubidium, cesium, yttrium, lanthanum, cerium,

praseodymium, neodymium, samarium, chromium, iron, cobalt, rhodium, nickel, copper, zinc, and mixtures thereof.

[0009] Dehydrofluorination catalysts include aluminum fluoride, fluorided alumina, metals on aluminum fluoride, and metals on fluorided alumina, as disclosed in U. S. Patent No. 5,396,000, incorporated herein by reference. Fluorided alumina and aluminum fluoride can be prepared as described in U. S. Patent No. 4,902,838, incorporated herein by reference. Suitable metals include chromium, magnesium (e.g., magnesium fluoride), Group VIIB metals (e.g., manganese), Group IIIB metals (e.g., lanthanum), and zinc. In use, such metals are normally present as halides (e.g., fluorides), as oxides and/or as oxyhalides. Metals on aluminum fluoride and metals on fluorided alumina can be prepared by procedures as described in U.S. Patent No. 4,766,260, incorporated herein by reference. In one embodiment, when supported metals are used, the total metal content of the catalyst is from about 0.1 to 20 percent by weight, typically from about 0.1 to 10 percent by weight. Preferred catalysts include catalysts consisting essentially of aluminum fluoride and/or fluorided alumina.

[0010] Additionally, dehydrofluorination catalysts include oxides, fluorides, and oxyfluorides of magnesium, zinc and mixtures of magnesium and zinc and/or aluminum. A suitable catalyst may be prepared, for example by drying magnesium oxide until essentially all water is removed, e.g., for about 18 hours at about 100°C. The dried material is then transferred to the reactor to be used. The temperature is then gradually increased to about 400°C while maintaining a flow of nitrogen through the reactor to remove any remaining traces of moisture from the magnesium oxide and the reactor. The temperature is then lowered to about 200°C and a fluoriding agent, such as HF, or other vaporizable fluorine containing compounds such as HF, SF_4, CCl_3F, CCl_2F_3, CHF_3, $CHClF_2$ or CCl_2FCClF_2, optionally diluted with an inert gas such as nitrogen, is passed through the reactor. The inert gas or nitrogen can be gradually reduced until only HF or other vaporizable fluorine

containing compounds is being passed through the reactor. At this point, the temperature can be increased to about 450°C and held at that temperature to convert the magnesium oxide to a fluoride content corresponding to at least 40 percent by weight, e.g., for 15 to 300 minutes, depending on the fluoriding agent flowrate and the catalyst volume. The fluorides are in the form of magnesium fluoride or magnesium oxyfluoride; the remainder of the catalyst is magnesium oxide. It is understood in the art that fluoriding conditions such as time and temperature can be adjusted to provide higher than 40 percent by weight fluoride-containing material.

[0011] Another suitable procedure for the catalyst preparation is to add ammonium hydroxide to a solution of magnesium nitrate and, if present, zinc nitrate and/or aluminum nitrate. The ammonium hydroxide is added to the nitrate solution to a pH of about 9.0 to 9.5. At the end of the addition, the solution is filtered, the solid obtained is washed with water, dried and slowly heated to 500°C, where it is calcined. The calcined product is then treated with a suitable fluorine-containing compound as described above.

[0012] Yet another procedure for the preparation of metal (i.e., magnesium, optionally containing also zinc and/or aluminum) fluoride catalysts containing one or more metal fluorides is to treat an aqueous solution of the metal(s) halide(s) or nitrate(s) in deionized water with 48 percent aqueous HF with stirring. Stirring is continued overnight and the slurry evaporated to dryness on a steam bath. The dried solid is then calcined in air at 400 °C for about four hours, cooled to room temperature, crushed and sieved to provide material for use in catalyst evaluations.

[0013] Additionally, dehydrofluorination catalysts include lanthanum oxide and fluorided lanthanum oxide.

[0014] Suitable fluorided lanthanum oxide compositions may be prepared in any manner analogous to those known to the art for the preparation of fluorided alumina. For example, the catalyst composition can be prepared by fluorination of lanthanum oxide.

[0015] Suitable catalyst compositions may also be prepared by precipitation of lanthanum as the hydroxide, which is thereafter dried and calcined to form an oxide, a technique well known to the art. The resulting oxide can then be pretreated as described herein.

[0016] The catalyst composition can be fluorinated to the desired fluorine content by pretreatment with a fluorine-containing compound at elevated temperatures, e.g., at about 200°C to about 450°C. The pretreatment with a vaporizable fluorine-containing compound such as HF, SF_4, CCl_3F, CCl_2F_3, CHF_3, $CHClF_2$ or CCl_2FCClF_2 can be done in any convenient manner including in the reactor which is to be used for carrying out the dehydrofluorination reaction. By vaporizable fluorine-containing compound is meant a fluorine containing compound which, when passed over the catalyst at the indicated conditions, will fluorinate the catalyst to the desired degree.

[0017] A suitable catalyst may be prepared, for example, by drying La_2O_3 until essentially all moisture is removed, e.g., for about 18 hours at about 400°C. The dried catalyst is then transferred to the reactor to be used. The temperature is then gradually increased to about 400°C while maintaining a flow of N_2 through the reactor to remove any remaining traces of moisture from the catalyst and the reactor. The temperature is then lowered to about 200°C and the vaporizable fluorine-containing compound is passed through the reactor. If necessary, nitrogen or other inert gases can be used as diluents. The N_2 or other inert diluents can be gradually reduced until only the vaporizable fluorine-containing compound is being passed through the reactor. At this point the temperature can be increased to about 450°C and held at that temperature to convert the La_2O_3 to a fluorine content corresponding to at least 80 percent LaF_3 by weight, e.g., for 15 to 300 minutes, depending on the flow of the fluorine containing compound and the catalyst volume.

[0018] Another suitable procedure for the catalyst preparation is to add ammonium hydroxide to a solution of $La(NO_3)_36H_2O$. The ammonium hydroxide is added to the nitrate solution to a pH of about 9.0 to 9.5. At

the end of the addition, the solution is filtered, the solid obtained is washed with water, and slowly heated to about 400 °C, where it is calcined. The calcined product is then treated with a suitable vaporizable fluorine-containing compound as described above.

[0019] Additionally, dehydrofluorination catalysts include chromium oxides, fluorided chromium oxides, and cubic chromium trifluoride. Cubic chromium trifluoride may be prepared from CrF_3XH_2O, where X is 3 to 9, preferably 4, by heating in air or an inert atmosphere (e.g., nitrogen or argon) at a temperature of about 350 °C to about 400 °C for 3 to 12 hours, preferably 3 to 6 hours.

[0020] Cubic chromium trifluoride is useful by itself, or together with other chromium compounds, as a dehydrofluorination catalyst. Preparation of cubic chromium trifluoride is described in U. S. Patent No. 6,031,141, incorporated herein by reference. Of note are catalyst compositions comprising chromium wherein at least 10 weight percent of the chromium is in the form of cubic chromium trifluoride, particularly catalyst compositions wherein at least 25 percent of the chromium is in the form of cubic chromium trifluoride, and especially catalyst compositions wherein at least 60 percent of the chromium is in the form of cubic chromium trifluoride. The chromium, including the cubic chromium trifluoride can be supported on and/or physically mixed with materials such as carbon, aluminum fluoride, fluorided alumina, lanthanum fluoride, magnesium fluoride, calcium fluoride, zinc fluoride and the like. Preferred are combinations including cubic chromium trifluoride in combination with magnesium fluoride and/or zinc fluoride.

[0021] Additionally, dehydrofluorination catalysts include activated carbon, or three dimensional matrix carbonaceous materials as disclosed in U. S. Patent No. 6,369,284, incorporated herein by reference; or carbon or metals such as sodium, potassium, rubidium, cesium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, chromium, iron, cobalt, rhodium, nickel, copper, zinc, and mixtures thereof, supported on carbon as disclosed in U. S. Patent No. 5,268,122, incorporated herein

by reference. Carbon from any of the following sources are useful for the process of this invention; wood, peat, coal, coconut shells, bones, lignite, petroleum-based residues and sugar. Commercially available carbons which may be used include those sold under the following trademarks: Barneby & Sutcliffe™, Darco™, Nucharm, Columbia JXN™, Columbia LCK™, Calgon PCB, Calgon BPL™, Westvaco™, Norit™, and Barnaby Cheny NB™.

[0022] Carbon includes acid-washed carbon (e.g., carbon which has been treated with hydrochloric acid or hydrochloric acid followed by hydrofluoric acid). Acid treatment is typically sufficient to provide carbon that contains less than 1000 ppm of ash. Suitable acid treatment of carbon is described in U.S. Patent No. 5,136,113, incorporated herein by reference. The carbon also includes three dimensional matrix porous carbonaceous materials. Examples are those described in U.S. Pat. No. 4,978,649, incorporated herein by reference. Of note are three dimensional matrix carbonaceous materials which are obtained by introducing gaseous or vaporous carbon-containing compounds (e.g., hydrocarbons) into a mass of granules of a carbonaceous material (e.g., carbon black); decomposing the carbon-containing compounds to deposit carbon on the surface of the granules; and treating the resulting material with an activator gas comprising steam to provide a porous carbonaceous material. A carbon-carbon composite material is thus formed.

[0023] The physical shape of the catalyst is not critical and may, for example, include pellets, powders or granules. Additionally, for catalysts supported on carbon, the carbon may be in the form of powder, granules, or pellets, or the like. Although not essential, catalysts that have not been fluorided may be treated with HF before use. It is thought that this converts some of the surface oxides to oxyfluorides. This pretreatment can be accomplished by placing the catalyst in a suitable container (which can be the reactor to be used to perform the reaction of the instant invention) and thereafter, passing HF over the dried catalyst so as to partially saturate the catalyst with HF. This is conveniently carried out by passing HF over the

catalyst for a period of time (e.g., about 15 to 300 minutes) at a temperature of, for example, about 200 °C to about 450 °C.

[0024] The catalytic dehydrofluorination may be suitably conducted at a temperature in the range of from about 200 °C to about 500 °C, and, in another embodiment, from about 300 °C to about 450 °C. The contact time is typically from about 1 to about 450 seconds, and, in another embodiment, from about 10 to about 120 seconds.

[0025] The reaction pressure can be subatmospheric, atmospheric or superatmostpheric. Generally, near atmospheric pressures are preferred. However, the dehydrofluorination can be beneficially run under reduced pressure (i.e., pressures less than one atmosphere).

[0026] The catalytic dehydrofluorination can optionally be carried out in the presence of an inert gas such as nitrogen, helium, or argon. The addition of an inert gas can be used to increase the extent of dehydrofluorination. Of note are processes where the mole ratio of inert gas to hydrofluorocarbon undergoing dehydrofluorination is from about 5:1 to about 1:1. Nitrogen is a preferred inert gas.

[0027] The reaction zone for catalyzed dehydrofluorination may be a reaction vessel fabricated from nickel, iron, titanium or their alloys, as described in U. S. Patent No. 6,540,933, incorporated herein by reference. A reaction vessel of these materials (e.g., a metal tube) optionally packed with the metal in suitable form may also be used. When reference is made to alloys, it is meant a nickel alloy containing from about 1 to about 99.9 weight percent nickel, an iron alloy containing about 0.2 to about 99.8 weight percent iron, and a titanium alloy containing about 72 to about 99.8 weight percent titanium. Of note is the use of an empty (unpacked) reaction vessel made of nickel or alloys of nickel such as those containing about 40 weight percent to about 80 weight percent nickel, e.g., Inconel™ 600 nickel alloy, Hastelloy™ C617 nickel alloy or Hastelloy™ C276 nickel alloy.

[0028] When used for packing, the metal or metal alloys may be particles or formed shapes such as, for example, perforated plates, rings, wire, screen, chips, pipe, shot, gauze, or wool.

[0029] The product mixture resulting from the dehydrofluorination of the hydrofluorocarbon blends will contain hydrofluoroolefins, unreacted hydrofluorocarbons and hydrogen fluoride. The amount and the relative proportions of unreacted hydrofluorocarbons will depend upon the percent conversion achieved in the reaction, as well as the composition of the hydrofluorocarbon blend. Unreacted hydrofluorocarbons can be recirculated back to the reaction zone for production of additional HFC-1225ye and HFC-1234yf. The product HFC-1225ye and HFC-1234yf may be recovered from the reaction product, hydrogen fluoride, and unreacted hydrofluorocarbons by conventional procedures such as distillation.

[0030] In one embodiment, the ratio of flurocarbons HFC-236ea and HFC-245eb fed to the reaction zone can be from about 10 : 1 to about 80 : 1. The ratio of the two fluorocarbons fed to the reaction zone will determine the ratio of HFC-1225ye to HFC-1234yf obtained from the product mixture. In another embodiment, the ratio of HFC-236cb and HFC-245eb fed to the reaction zone is from about 35 : 1 to about 80 : 1.

[0031] The following Examples are meant to illustrate the invention and are not meant to be limiting.

EXAMPLE 1

Dehydrofluorination of $CF_3CHFCHF_2$ and CF_3CHFCH_2F to $CF_3CF=CHF$ (*E* and *Z* isomers) and $CF_3CF=CH_2$ over carbonaceous catalyst

[0032] A mixture of $CF_3CHFCHF_2$, CF_3CHFCH_2F (mole ratio 30:1) and nitrogen are passed through the reactor as follows. A Hastelloy™ nickel alloy reactor (2.54 cm OD X 2.17 cm ID X 24.1 cm L) is charged with 14.32 g (25 mL) of spherical (8 mesh) three dimensional matrix porous carbonaceous material prepared substantially as described in U.S. Patent No. 4,978,649, incorporated herein by reference. The packed portion of the reactor is heated by a 5" X 1" ceramic band heater clamped

to the outside of the reactor. A thermocouple positioned between the reactor wall and the heater measures the reactor temperature. After charging the reactor with the carbonaceous material, nitrogen (10 ml/min, $1.7X10^{-7}$ m^3/s) is passed through the reactor and the temperature is raised to 200 °C during a period of one hour and maintained at this temperature for an additional 4 hours. At a temperature of 350°C, 10 sccm of nitrogen ($1.7 x10^{-7}$ m^3/s) and 15 sccm ($2.5 x10^{-7}$ m^3/s) of a blend of $CF_3CHFCHF_2/CF_3CHFCH_2F$ are mixed and flowed through the reactor. The temperature is then raised to 400°C, and the flow rates held constant. The effluent for both temperatures is sampled and analyzed by ^{19}F NMR. A portion of the total reactor effluent is sampled on-line for organic product analysis using a gas chromatograph equipped with a mass selective detector (GC-MS); the results are summarized in Table 1. The bulk of the reactor effluent containing organic products and also inorganic acid, such as HF, is treated with aqueous caustic for neutralization

TABLE 1

Temp., °C	N_2 flow (sccm)	HFC flow (sccm)	Concentrations, (Mole %)		
			$CF_3CF=CH_2$	$CF_3CF=CHF$	Unks
350	10	15	57.8	39.2	3.0
400	10	15	55.5	37.7	6.8

Unks = unknowns

EXAMPLE 2

Synthesis of $CF_3CF=CH_2$ and $CF_3CF=CHF$ with Fluorided Alumina

[0033] A 15 in (38.1 cm) x 3/8 in (0.95 cm) Hastelloy tube is charged with 7.96 grams (13cc) of gamma-alumina ground to 12-20 mesh (0.84 to 1.68 mm). The catalyst is activated by heating at 200°C for 15 minutes under a nitrogen purge (50 sccm, $8.3x10^{-7}$ m^3/s). The temperature is raised to 325°C for 10 minutes, to 400°C for 20 minutes, and then lowered

to 300°C for 60 minutes. The nitrogen flow is reduced to 35 sccm (5.8×10^{-7} m^3/s) and anhydrous HF vapor is fed at 12 sccm (2.0×10^{-7} m^3/s) for 35 minutes. The temperature is then raised to 325°C for 60 minutes, to 350°C for 60 minutes, to 375°C for 90 minutes, to 400°C for 30 minutes, and to 425°C for 40 minutes. The nitrogen flow is then reduced to 25 sccm (4.2×10^{-7} m^3/s) and the HF raised to 20 sccm (3.3×10^{-7} m^3/s) for 20 minutes. The nitrogen flow is then reduced to 15 sccm (2.5×10^{-7} m^3/s) and the HF flow increased to 28 sccm (4.7×10^{-7} m^3/s) for 20 minutes. The nitrogen flow is then reduced to 5 sccm (8.3×10^{-8} m^3/s) and the HF increased to 36 sccm (6.0×10^{-7} m^3/s) for 20 minutes. The nitrogen flow is then shut off, and the HF flow increased to 40 sccm (6.7×10^{-7} m^3/s) for 121 minutes.

[0034] The temperature of the reactor is set to 400 °C, and a mixture of 10 sccm (1.7×10^{-7} m^3/s) of nitrogen and 15 sccm (2.5×10^{-7} m^3/s) of various blends of $CF_3CHFCHF_2$ and CF_3CHFCH_2F are passed through the reactor giving a contact time of 60 seconds. The flows are reduced to 5 sccm 8.3×10^{-8} m^3/s) of nitrogen (and 7.5 sccm (1.3×10^{-7} m^3/s) of HFC giving a contact time of 120 seconds. The effluent is sampled under both sets of conditions and analyzed by ^{19}F NMR. The effluent compositions as determined by GC are listed in Table 2.

TABLE 2

Temp., °C	N_2 flow (sccm)	236ea:245eb ratio	HFC Flow (sccm)	Concentrations, Mole%		
				$CF_3CF=CH_2$	$CF_3CF=CHF$	Unk
400	5	10:1	7.5	85.6	11.9	2.5
400	5	30:1	7.5	58.0	39.3	2.7
400	5	50:1	7.5	44.3	54.2	1.5
400	5	80:1	7.5	30.2	68.6	1.2

Unks = unknowns

Example 3

Synthesis of $CF_3CF=CH_2$ and $CF_3CF=CHF$ with Fluorided Alumina

[0035] A 15 in (38.1 cm) x 3/8 in (0.95 cm) Hastelloy tube was charged with 7.87 grams (13cc) of gamma-alumina ground to 12-20 mesh (0.84 to 1.68 mm). The catalyst was activated by heating at 200°C for 15 minutes under a nitrogen purge (50 sccm, 8.3x10-7 m^3/s). The temperature was raised to 325°C for 10 minutes, to 400°C for 20 minutes, and then lowered to 300°C for 60 minutes. The nitrogen flow was reduced to 35 sccm (5.8x10-7 m3/s) and anhydrous HF vapor was fed at 12 sccm (2.0x10-7 m^3/s) for 35 minutes. The temperature was then raised to 325°C for 60 minutes, to 350°C for 60 minutes, to 375°C for 90 minutes, to 400°C for 30 minutes, and to 425°C for 40 minutes. The nitrogen flow was then reduced to 25 sccm ($4.2x10^{-7}$ m^3/s) and the HF raised to 20 sccm ($3.3 x10^{-7}$ m^3/s) for 20 minutes. The nitrogen flow was then reduced to 15 sccm ($2.5x10^{-7}$ m^3/s) and the HF flow increased to 28 sccm ($4.7 x10^{-7}$ m^3/s) for 20 minutes. The nitrogen flow was then reduced to 5 sccm ($8.3x10^{-8}$ m^3/s) and the HF increased to 36 sccm ($6.0 x10^{-7}$ m^3/s) for 20 minutes. The nitrogen flow was then shut off, and the HF flow increased to 40 sccm ($6.7 x10^{-7}$ m^3/s) for 121 minutes.

[0036] The temperature of the reactor was set to 375 °C, and a mixture of 13 sccm ($2.2 x10^{-7}$ m^3/s) of a blend of $CF_3CHFCHF_2$ and CF_3CHFCH_2F in a 9:1 mole ratio were passed through the reactor giving a contact time of 60 seconds. The effluent compositions as determined by GCMS are listed in Table 3 below in mole%.

TABLE 3

1234yf	Z-1225ye	1234ze	E-1225ye	236ea	245eb
8.85	17.55	1.3%	2.2%	69.8%	0.3%

[0037] While specific embodiments of the invention have been shown and described, further modifications and improvements will occur to

those skilled in the art. It is desired that it be understood, therefore, that the invention is not limited to the particular form shown and it is intended in the appended claims which follow to cover all modifications which do not depart from the spirit and scope of the invention.

CLAIM(S)

What is claimed is :

1. A process for the co-manufacture of 1,2,3,3,3-pentafluoropropene and 2,3,3,3-tetrafluoropropene comprising:

   dehydrofluorinating a blend of 1,1,1,2,3,3-hexafluoropropane and 1,1,1,2,3-pentafluoropropane in a reaction zone having a catalyst, thereby forming a product mixture comprising said 1,2,3,3,3-pentafluoropropene and 2,3,3,3-tetrafluoropropene, unreacted hydrofluorocarbons and hydrogen fluoride, and separating said blend of 1,2,3,3,3-pentafluoropropene and 2,3,3,3-tetrafluoropropene from hydrogen fluoride and said unreacted hydrofluorocarbons to produce 1,2,3,3,3-pentafluoropropene and 2,3,3,3-tetrafluroropropene.

2. A process as in claim 1 further comprising recirculating the unreacted hydrofluorocarbons back to the reaction zone.

3. A process as in claim 1 wherein the process is carried out at a temperature of from about 200 °C to about 500 °C.

4. A process as in claim 1 wherein the catalyst is selected from the group consisting of aluminum fluoride, fluorided alumina, and metals on fluorided alumina.

5. A process as in claim 4 wherein the catalyst is aluminum fluoride.

6. A process as in claim 1 wherein the process is carried out in the presence of an inert gas.

7. A process as in claim 6 wherein the inert gas is nitrogen.

8. A process as in claim 1 wherein the mole ratio of 1,1,1,2,3,3-hexafluoropropane and 1,1,1,2,3-pentafluoropropane fed to the reaction zone is from about 10 : 1 to about 80 : 1.

9. A process as in claim 8 wherein the mole ratio of 1,1,1,2,3,3-hexafluoropropane and 1,1,1,2,3-pentafluoropropane fed to the reaction zone is from about 35 : 1 to about 80 : 1.

10. A process as in claim 1 wherein the hydrofluoroolefins are separated from the hydrogen fluoride and the hydrofluorocarbons by distillation.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/008202

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C17/25 C07C21/18

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 practical, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94/27940 A (DU PONT [US]) 8 December 1994 (1994-12-08) claims 1-10; examples 1,2	1-10
P,A	WO 2007/019358 A (DU PONT [US]; RAO VELLIYUR NOTT MALLIKARJUNA [US]; SIEVERT ALLEN C [US) 15 February 2007 (2007-02-15) claims 1-4	1-10

☐ 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 document but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 August 2007	05/09/2007

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Kleidernigg, Oliver

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2007/008202

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9427940 A	08-12-1994	AU 6914894 A	20-12-1994
		EP 0700372 A1	13-03-1996
		JP 8510739 T	12-11-1996
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WPI ACC NO: 1991-246878/ **199134**
XRAM Acc No: C1991-107124
Prepn. of satd. fluorocarbon(s) free from chlorine - by catalytic hydrogenation of unsatd. hydrocarbon(s) contg. fluorine and chlorine
Patent Assignee: BAYER AG (FARB)
Inventor: BIELEFELDT D; BRADEN R; NEGELE M; ZIEMANN H
Patent Family (10 patents, 10 countries)

Patent Number	Kind	Date	Application Number	Kind	Date	Update	
EP 442087	A	19910821	EP 1990124183	A	19901214	199134	B
DE 4004494	A	19910822	DE 4004494	A	19900214	199135	E
CA 2036221	A	19910815				199143	E
JP 4211026	A	19920803	JP 199138038	A	19910207	199237	E
EP 442087	B1	19931208	EP 1990124183	A	19901214	199349	E
DE 59003798	G	19940120	DE 59003798	A	19901214	199404	E
			EP 1990124183	A	19901214		
ES 2059976	T3	19941116	EP 1990124183	A	19901214	199501	E
JP 1995106996	B2	19951115	JP 199138038	A	19910207	199550	E
US 5530169	A	19960625	US 1991651846	A	19910204	199631	E
			US 1991759793	A	19910913		
			US 1994326143	A	19941019		
CA 2036221	C	20010424	CA 2036221	A	19910212	200128	E

Priority Applications (no., kind, date): DE 4004494 A 19900214

Patent Details

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Regional Designated States,Original: BE DE ES FR GB IT NL					
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EP 442087	B1	DE	5	0	
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DE 59003798	G	DE			Application EP 1990124183 Based on OPI patent EP 442087
ES 2059976	T3	ES			Application EP 1990124183 Based on OPI patent EP 442087
JP 1995106996	B2	JA	4	0	Based on OPI patent JP 04211026
US 5530169	A	EN			Continuation of application US 1991651846 Continuation of application US 1991759793
CA 2036221	C	EN			

Alerting Abstract EP A
Satd. fluoro-hydrocarbons, free from Cl, of formula Rf-CH2CH2-Rf (I) are prepd. by catalytic, gas-phase hydrogenation of unsatd. hydrocarbons contg. F and Cl, of formula Rf-CX=CCl-Rf (II), at above 80 deg. C. In formulae, Rf = -(-CF2-)n-CF3, or the 2 Rf's together form -CF2CF2CF2-; n = 0-7; and the 2 n values together are not above 10. Reaction is pref. at 90-400 (95-250) deg. C and 1-20 bars, using a molar ratio of (II):H2 of 1:3-50, and a flow rate such that the catalyst loading is 20-2,000 g/l/h. The catalyst is a supported transition metal, esp. Pd or Pt on C, Al2O3, SiO2, BaSO4, spinels, silicates or TiO2.

USE/ADVANTAGE - (I) are insulating and blowing gases for synthetic foams, not damaging the O3 layer, and operating fluids for heat pump systems. Conversion and selectivity are above 80%, often above 90%.

USE/ADVANTAGE - In an example, 0.37 mols/hr of CF3-CH=CCl-CF3 and 2.5 mols./hr of H2 were led at 150 deg. C, normal pressure, and a catalyst loading of 360 g/l/hr over a catalyst contg. Pd on Li-Al spinel (18 g/l). Conversion was 91%, and selectivity for CF3-CH2CH2-CF3 was 78%. @(4pp Dwg.No 0/0)

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(71) Applicant: **DAIKIN INDUSTRIES, LIMITED**
Osaka-shi Osaka 530 (JP)

(72) Inventors:
- **Aoyama, Hirokazu,**
  c/o Daikin Industries Ltd.
  Settsu-shi, Osaka 566 (JP)
- **Seki, Eiji,**
  c/o Daikin Industries Ltd.
  Settsu-shi, Osaka 566 (JP)

(74) Representative: **TER MEER - MÜLLER - STEINMEISTER & PARTNER**
Mauerkircherstrasse 45
81679 München (DE)

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This application was filed on 04 - 04 - 1996 as a divisional application to the application mentioned under INID code 62.

(54) Method for manufacturing 1,1,1,2,3-pentafluoropropene and method for manufacturing 1,1,1,2,3-pentafluoropropane

(57) The present invention provides manufacturing methods of 1,1,1,2,3-pentafluoropropene characterized by the reaction of removing HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gas state with trivalent chromium oxide or partly fluorinated trivalent chromium oxide. 1,1,1,2,3-pentafluoropropene can be produced from easily available 1,1,1,2,3,3-hexafluoropropane by cost-effective industrial methods at high yields according to the invention.

The inventions also provide manufacturing methods of 1,1,1,2,3-pentafluoropropane characterized by reducing 1,1,1,2,3-pentafluoropropene with hydrogen under the presence of a hydrogenation catalyst consisting of palladium added with one or more of silver, copper, gold, tellurium, zinc, chromium, molybdenum, and thallium or under the presence of a rhodium catalyst. The desired product can be produced at high reactivities and high selectivities according to the invention.

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Description

Fields of Industrial Application

The present inventions relate to methods for manufacturing 1,1,1,2,3-pentafluoropropene, which is useful as an intermediate for compounds that can be substitutes for CFC and HCFC as refrigerants, blowing agents and cleaning agents, and as a monomer of macromolecule compounds, and methods for manufacturing 1,1,1,2,3-pentafluoropropane, which is a useful compound that can be said substitutes for CFC and HCFC for said uses.

Conventional Methods

Among the conventionally known manufacturing methods of 1,1,1,2,3-pentafluoropropene are: 1) the method of 1,1,1,2,3,3-hexafluoropropane (which is produced by hydrogenating hexafluoropropene) being reacted with an aqueous solution of KOH with a 70% to 80% concentration at 150°C (Ann. Chim. (Italy) vol. 55, 850p, 1965); and 2) the method of 1,1,1,2,3,3-hexafluoropropane being reacted with KOH in dibutylether (Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1412p, 1960). Another known method is: the method of removing HF from 1,1,1,2,3,3-hexafluoropropane by means of granular KCl in the gaseous phase at 700°C to produce the desired product (Ann. Chim. (Italy) vol. 55, 850p, 1965).

Those methods, however, contained in the above-mentioned literature are not cost-effective because a large amount of alkali is used. As to the gaseous reaction process with KCl, it does not suit to the industrial production because it produces a 30% large amount of 1,1,1,3,3-pentafluoropropene having a boiling point approximate to that of 1,1,1,2,3-pentafluoropropene and being difficult to be separate by the ordinary rectification methods cannot well separate away.

The known manufacturing method of 1,1,1,2,3-pentafluoropropane is the method of hydrogenating 1,1,1,2,3-pentafluoropropene as a raw material (Izvest. Akad. Nauk S.S.S.R. 1960, 1412-18).

This method, however, has a low yield because it also further hydrogenates the material and produces 1,1,1,2-tetrafluoropropane. The method does not suit to the industrial production because 1,1,1,2-tetrafluoropropane, which is azeotropic or pseudo-azeotropic with 1,1,1,2,3-pentafluoropropane, is difficult to separate.

Objectives of the Inventions

An objective of the present inventions is to provide a highly cost-effective industrial method to produce 1,1,1,2,3-pentafluoropropene at high yields.

The other objective of those inventions is to provide a method with high reactivities and selectivities to produce 1,1,1,2,3-pentafluoropropane.

Contents of the Inventions

The inventors have thoroughly studied cost-effective industrial production methods of 1,1,1,2,3-pentafluoropropene, particularly those by means of the reaction to remove hydrogen fluroride from 1,1,1,2,3,3-hexafluoropropane which is obtained by hydrogenating hexafluoropropene, which is easily available.

The inventors have discovered that the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with trivalent chromium oxide or partly fluorinated trivalent chromium oxide causes a reaction to remove HF to produce 1,1,1,2,3-pentafluoropropene at high yields. The invention has been achieved based on this discovery.

That is, the first aspect of the invention relates to a method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction to remove HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with trivalent chromium oxide or partly fluorinated trivalent chromium oxide.

The inventors have discovered that the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with either chromium (III) oxides or partly fluorinated chromium (III) oxides under the presence of oxygen causes a reaction to remove HF to produce 1,1,1,2,3-pentafluoropropene at high yields, and that the catalyst for this process tends to retain activity longer and have a longer life. The invention has been achieved based on this discovery.

That is, the second aspect of the invention relates to a method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction to remove HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with either chromium (III) oxides or partly fluorinated chromium (III) oxides under the presence of oxygen.

For the second aspect of the invention, it is essential to make 1,1,1,2,3,3-hexafluoropropane in the gaseous state contact with either chromium (III) oxides or partly fluorinated chromium (III) oxides under the presence of oxygen. This is in practice a form of vapor phase reaction in which, for example, 1,1,1,2,3,3-hexafluoropropane in the gaseous state is made flow through a reaction tube filled with either chromium (III) oxides or partly fluorinated chromium (III) oxides at

a specific temperature. The methods of the vapor-phase reaction can be the fixed-bed reaction, the fluid-bed reaction and so on.

For this invention, any preparation method of a catalyst comprising chromium (III) oxides or partly fluorinated chromium (III) oxides is acceptable. Chromium oxide can, for example, be prepared by reducing CrO_3 or by obtaining precipitate from a salt of Cr^{3+}.

A catalyst in the state of hydrate should be dried at 120°C to 300°C and then calcinated ordinarily at 300°C to 600°C or preferably at 350°C to 450°C.

The treatment to fluorinate (or activate) a catalyst should be conducted ordinarily at 20°C to 450°C or preferably at 200°C to 400°C for the purpose. That fluorination can be conducted, for example, with hydrogen fluoride anhydride in the fluorination reaction system or by means of the heating treatment with fluorinated hydrocarbon. Partly fluorinated chromium (III) oxide can be obtained by heating a CrF_3 hydrate with oxygen.

The appropriate reaction temperature and contact time are 200°C to 600°C (or more appropriately 250°C to 500°C) and 0.1 second to 300 seconds (or more appropriately 0.5 second to 120 seconds), respectively, as in the above.

The concentration of oxygen present in said reaction of removing HF can be largely varied, but should ordinarily 0.005% to 20% of the total flow or preferably 0.01% to 10% of the total flow. An oxygen-containing mixed gas such as air can be used in the reaction process. In such a case, the gas concentration must comply with the above criterion figures for oxygen concentration.

The inventors have thoroughly studied production methods of 1,1,1,2,3-pentafluoropropane through vapor-phase catalytic reduction with a palladium catalyst, especially the methods that do not cause the problems mentioned in the above. As a result, they have discovered that hydrogenating 1,1,1,2,3-pentafluoropropene as obtained through the methods mentioned above as the raw material in the vapor or liquid phase under the presence of a palladium alloy catalyst at particularly 0°C to 550°C is an industrially easy manufacturing method of 1,1,1,2,3-pentafluoropropane with high yields to achieve the objective with high selectivity and high yields. The invention has been achieved based on this discovery.

That is, the third aspect of the invention is in a method for manufacturing 1,1,1,2,3-pentafluoropropane characterized by the reduction of 1,1,1,2,3-pentafluoropropene as obtained by the methods mentioned above with hydrogen under the presence of a hydrogenation catalyst consisting of palladium added with one or more metals selected from silver, copper, gold, tellurium, zinc, chromium, molybdenum, and thallium.

For the third aspect of the invention, it is essential to add other metal(s) to palladium.

An alloy catalyst is generally considered to show the characteristics of the each constituent element according to its composition. For the invention, the amount of added metallic constituents to palladium should appropriately be 0.01 weight% to 500 weight%, or optimally 0.1 weight% to 300 weight% to take the advantage of the characteristics of palladium.

The acceptable amount of the carrying concentration of palladium alloy on various kinds of carriers is from 0.05% to 10%, but the recommended range is ordinarily 0.5% to 2%.

For the third aspect of the invention, the appropriate carriers of palladium alloy catalysts are active carbon, alumina, silica gel, zirconia, titania, and so on.

The particle size of the carrier is preferably 0.1 mm to 100 mm although it has little effect on the reaction.

The ratio of hydrogen and the raw material in the 1,1,1,2,3-pentafluoropropene hydrogenation reaction can be largely varied. The reaction should, however, be ordinarily conducted with at least a stoichiometric amount of hydrogen. An amount of hydrogen, such as 4 mol or more, which is far more than the stoichiometric one can be used for the whole mol of the starting material.

The reaction should be conducted in the liquid or vapor phase. The methods of the vapor-phase reaction can be the fixed-bed reaction, the fluid-bed reaction and so on.

There are no restrictions on the reaction pressure so that the reaction can be conducted under a high pressure, a reduced pressure and the atmospheric pressure. It is preferable to conduct the reaction under a high pressure or the atmospheric pressure because the reduced pressure requires more complicated devices.

The appropriate reaction temperature is 0°C to 550°C, and 50°C to 450°C for the vapor phase reaction.

For the vapor phase reaction, the contact time is ordinarily 0.1 second to 300 seconds or more appropriately 1 second to 30 seconds.

The material 1,1,1,2,3-pentafluoropropene used as the raw material for the method of the third aspect of the invention can be synthesized through the methods of the invention as mentioned above.

The inventors have thoroughly studied production methods of 1,1,1,2,3-pentafluoropropane to solve the problems mentioned in the above. As a result, they have discovered that hydrogenating 1,1,1,2,3-pentafluoropropene as the raw material in the vapor phase under the presence of a rhodium catalyst brings about obtaining the target product at high yields. The invention has been achieved based on this discovery.

That is, the fourth aspect of the invention relates to a method for manufacturing 1,1,1,2,3-pentafluoropropane especially at a 97% or more high yield by means of the hydrogenation reaction on 1,1,1,2,3-pentafluoropropene as the starting material under the presence of a rhodium catalyst especially at 30°C to 450°C.

For the fourth aspect of the invention, it is essential to hydrogenate the material in the vapor phase by means of a rhodium catalyst. The methods of the vapor-phase reaction can be the fixed-bed reaction, the fluid-bed reaction and so on.

The rhodium catalysts are preferably supported on one or more carriers selected from active carbon, alumina, silica gel, titanium oxide, zirconia, and so on.

The particle size of the carrier is preferably 0.1 mm to 100 mm although it has little effect on the reaction.

The acceptable amount of the carrying concentration of rhodium is from 0.05 weight% to 10 weight%, but the recommended range is ordinarily 0.5 weight% to 5 weight%.

The appropriate reaction temperature is ordinarily 30°C to 450°C or more appropriately 70°C to 250°C.

For the fourth aspect of the invention, the ratio of hydrogen and the raw material for the 1,1,1,2,3-pentafluoropropene hydrogenation reaction can be largely varied. The reaction should, however, be ordinarily conducted with at least a stoichiometric amount of hydrogen. An amount of hydrogen, such as 2 mol or more, which is far more than the stoichiometric, one can be used for the whole mol of the starting material.

There are no restrictions on the reaction pressure so that the reaction can be conducted under a high pressure, a reduced pressure and the atmospheric pressure. It is preferable to conduct the reaction under a high pressure or the atmospheric pressure because the reduced pressure requires more complicated devices.

The contact time is ordinarily 0.1 second to 300 seconds or more appropriately 1 second to 30 seconds.

Industrial Applicability

The present inventions make it possible to produce 1,1,1,2,3-pentafluoropropene, which is useful as an intermediate of useful compounds that can be substitutes for CFC and HCFC as refrigerants, blowing agents and cleaning agents, and as a monomer of macromolecule compounds from easily available 1,1,1,2,3,3-hexafluoropropane, by cost-effective industrial methods with high yields.

They also make it possible to produce 1,1,1,2,3-pentafluoropropane at high yields and high selectivities by reducing with hydrogen 1,1,1,2,3-pentafluoropropene under the presence of a rhodium catalyst or of a hydrogenation catalyst created by adding palladium with one or more metals selected from silver, copper, gold, tellurium, zinc, chromium, molybdenum, and thallium.

Embodiments

The inventions are more specifically explained with their embodiments hereunder.

Embodiment 1

Chromium hydroxide prepared from an aqueous solution of chromium nitrate and aqueous ammonia was filtrated, washed with water, and dried at 100°C. The resulted material was shaped into a cylinder of 3 mm inner diameter and 3 mm height by means of a tapping forming machine. The obtained catalyst was filled into a Hastelloy C reaction tube before the reaction and was activated by heating it at a constant temperature 400°C in a nitrogen gas flow for 1 hour. Then, after the temperature was lowered down to 200°C, the catalyst was fluorinated by treating it with a supply of hydrogen fluoride anhydride diluted with N_2 for 5 hours.

10 g of the prepared catalyst was filled into a Hastelloy C reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 350°C while flowing nitrogen gas through it.

Then 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 30 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 1 shows the results.

Embodiment 2

10 g of the catalyst prepared according to the procedures in Embodiment 1 before the hydrogen fluoride anhydride treatment was filled into a Hastelloy C reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 400°C while nitrogen gas was flowed through it.

Then 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 40 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 1 shows the results.

Embodiment 3

Chromium hydroxide prepared from an aqueous solution of chromium nitrate and aqueous ammonia was filtrated, washed with water, and dried at 100°C. The resulted material was shaped into a cylinder of 3 mm diameter and 3 mm height by means of a tapping forming machine. The obtained catalyst was filled into a Hastelloy C reaction tube before the reaction and was heated at a constant temperature 400°C in a nitrogen gas flow for 1 hour. Then, after the temperature was lowered down to 200°C, the catalyst was activated by treating it with a supply of hydrogen fluoride anhydride for 1 hours.

20 g of the prepared catalyst was filled into a Hastelloy C reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 350°C while flowing nitrogen gas through it.

Then 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 57 cc/min with oxygen flowed at 3 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 2 shows the conversion rate and selectivity 1 hour after the start of the reaction and those 100 hours after that.

Embodiment 4

20 g of the catalyst prepared according to the procedures in Embodiment 3 was filled into a Hastelloy C reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 350°C while nitrogen gas was flowed through it.

Then 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 54 cc/min with air flowed at 6 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 2 shows the conversion rate and selectivity 1 hour after the start of the reaction and those 100 hours after that.

Embodiment 5

20 g of the catalyst prepared according to the procedures in Embodiment 3 was filled into a Hastelloy C reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 350°C while nitrogen gas was flowed through it.

Then 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 60 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 2 shows the conversion rate and selectivity 1 hour after the start of the reaction and those 100 hours after that.

Table 1

	Conversion (%)	Selectivity (%)
Embodiment 1	95.1	99.3
Embodiment 2	90.0	99.2

Table 2

	1 hour after the reaction started		100 hours after the reaction started	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
Embodiment 3	85.4	99.7	85.1	99.6
Embodiment 4	85.3	99.8	85.1	99.6
Embodiment 5	85.1	99.8	45.2	99.5

The results of the embodiments described above clearly demonstrate that 1,1,1,2,3-pentafluoropropene is obtained from easily available 1,1,1,2,3,3-hexafluoropropane by a cost-effective industrial method with high yields in accordance with the present inventions.

Embodiment 6

Palladium catalyst carried by active carbon at a 0.5% concentration was added to an aqueous solution of $CuCl_2$ of 0.1% concentration as Cu to the active carbon and was dropped with 0.2 ml of formalin. After the resulted substance was heated at 50°C for 5 hours, it was distilled to remove water under reduced pressure and then it was dried for 24hours at 100°C.

18 cc of the obtained catalyst was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length, and the tube was heated in an electric furnace at 350°C for 3 hours while hydrogen gas was flowed through it at 40 cc/min. Then, after the temperature was lowered down to an appropriate level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced into the tube at 20 cc/min with hydrogen introduced at 40 cc/min. The reaction temperature was 80°C.

The produced gas, which contains 1,1,1,2,3-pentafluoropropane, was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 3 shows the results.

Embodiment 7

Palladium catalyst carried by active carbon at a 0.5% concentration was added with silver by the use of $AgNO_3$ at a 0.1% concentration as Ag to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 6. Then the same reaction as Embodiment 6 was conducted. Table 3 shows the results.

Embodiment 8

Palladium catalyst carried by active carbon at a 0.5% concentration was added with tellurium by the use of $TeCl_2$ at a 0.1% concentration as Te to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 6. Then the same reaction as Embodiment 6 was conducted. Table 3 shows the results.

Embodiment 9

Palladium catalyst carried by active carbon at a 0.5% concentration was added with gold by the use of $AuCl_3$ at a 0.1% concentration as Au to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 6. Then the same reaction as Embodiment 6 was conducted. Table 3 shows the results.

Embodiment 10

Palladium catalyst carried by active carbon at a 0.5% concentration was added with zinc by the use of $ZnCl_2$ at a 2% concentration as Zn to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 6. The obtained alloy catalyst was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length, and the tube was heated in an electric furnace at 350°C while hydrogen gas was flowed through it at 40 cc/min.

Then, after the temperature was lowered down to a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced into the tube at 40 cc/min with hydrogen introduced at 80 cc/min. The reaction temperature was 100°C.

The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 3 shows the results.

Embodiment 11

Palladium catalyst carried by active carbon at a 0.5% concentration was added with chromium by the use of $Cr(NO_3)_3 \cdot 9H_2O$ at a 2% concentration as Cr to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 6. 17cc of the obtained alloy catalyst was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length, and the tube was heated in an electric furnace at 400°C while hydrogen gas was flowed through it.

Then, after the temperature was lowered down to a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced into the tube at 30 cc/min with hydrogen introduced at 60 cc/min. The reaction temperature was 100°C.

The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 3 shows the results.

Embodiment 12

Palladium catalyst carried by active carbon at a 0.5% concentration was added with thallium by the use of $TlCl_3$ at a 2% concentration as Tl to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 6. 15cc of the obtained alloy catalyst was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length, and the tube was heated in an electric furnace at 350°C while hydrogen gas was flowed through it at 40 cc/min.

Then, after the temperature was lowered down to a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced into the tube at 40 cc/min with hydrogen introduced at 80 cc/min. The reaction temperature was 150°C.

The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 3 shows the results.

Embodiment 13

Palladium catalyst carried by active carbon at a 0.5% concentration was added with molybdenum by the use of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ at a 2% concentration as Mo to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 6. 15 cc of the obtained alloy catalyst was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length, and the tube was heated in an electric furnace at 350°C while hydrogen gas was flowed through it at 40 cc/min.

Then, after the temperature was lowered down to a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced into the tube at 30 cc/min with hydrogen introduced at 60 cc/min. The reaction temperature was 120°C.

The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 3 shows the results.

Embodiment 14

Palladium catalyst carried by powdered active carbon at a 5% concentration was added with an aqueous solution of $AgNO_3$ of 1% concentration against the active carbon and then was added with 0.2 ml of formalin. After the resulted substance was heated for 5 hours at 50°C, it was distilled to remove water under reduced pressure. Analysis showed that the obtained catalyst contained 54% of water.

1 g of the obtained catalyst was put in an SUS316 autoclave of 200 cc. After the nitrogen substitution, 10 g of 1,1,1,2,3-pentafluoropropene was introduced into the autoclave. Then hydrogen gas was introduced until its amount reaches 9 kg/cm^2 at a room temperature while stirring. Hydrogen gas was added each time it was consumed and the reaction was maintained until hydrogen gas was not consumed any more. The reaction temperature was held at 25°C or under.

After the reaction finished, the reaction liquid was analyzed by gas chromatography. Table 3 shows the results.

Table 3

Embodiment No.	Conversion (%)	Selectivity (%)
6	99	98
7	99	98
8	99	96
9	99	98
10	98	97
11	99	97
12	98	96
13	98	96
14	99	98

The above results demonstrate that hydrogenation reaction according to the present inventions can produce the desired product at high conversion and high selectivity.

Embodiment 15

10 cc of a rhodium catalyst carried by alumina at 0.5% concentration was filled in an SUS316 reaction tube of 2 cm inner diameter and 40 cm length. Then the tube was heated in an electric furnace at 80°C while nitrogen gas was flowed through the tube.

After the tube temperature reached a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced at 26.7 cc/min with hydrogen introduced at 55.3 cc/min. The reaction temperature was held at 80°C. The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 4 shows the results.

Embodiment 16

18 cc of a rhodium catalyst carried by active carbon at 0.5% concentration was filled into the same reaction device as Embodiment 15. Then the device was heated in an electric furnace at 120°C while nitrogen gas was flowed through the tube.

After the tube temperature reached a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced at 40 cc/min with hydrogen introduced at 80 cc/min. The reaction temperature was held at 120°C. The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 5 shows the results.

Table 5

Embodiment No.	Conversion (%)	Selectivity (%)
15	100	99
16	100	99

The above results demonstrate that reaction according to the present inventions can produce the desired product 1,1,1,2,3-pentafluoropropane at high yields.

Claims

1. A method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction of removing HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with trivalent chromium oxide or partly fluorinated trivalent chromium oxide.

2. A method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction of removing HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with trivalent chromium oxide or partly fluorinated trivalent chromium oxide under the presence of oxygen.

3. A method for manufacturing 1,1,1,2,3-pentafluoropropane characterized by the reaction of the reduction of 1,1,1,2,3-pentafluoropropene as obtained by the method of claim 1 or 2 with hydrogen under the presence of a hydrogenation catalyst consisting of palladium added with one or more of metal selected from silver, copper, gold, tellurium, zinc, chromium, molybdenum, and thallium.

4. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to claim 3 wherein at least a stoichiometric amount of hydrogen to 1,1,1,2,3-pentafluoropropene is used.

5. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to claim 3 or 4 wherein the reaction is conducted at 0°C to 550°C.

6. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 3 to 5 wherein an alloy catalyst with a 0.01 weight% to 500 weight% concentration of an added metal constituent against the palladium concentration is used.

7. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 3 to 6 wherein a hydrogenation catalyst is used which is a catalyst consisting of palladium added with one or more of silver, copper, gold, tellurium, zinc, chromium, molybdenum and thallium and being carried by active carbon carrier.

8. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 3 to 7 wherein a hydrogenation catalyst is used which is a catalyst consisting of palladium added with one or more of silver, copper, gold, tellurium, zinc, chromium, molybdenum and thallium and being carried by at least one carrier of active carbon, alumina, silica gel, titanium oxide and zirconia.

9. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 3 to 8 wherein the carrying concentration of a palladium alloy catalyst on the carrier is 0.05% to 10%.

10. A method for manufacturing 1,1,1,2,3-pentafluoropropane characterized by the reaction of 1,1,1,2,3-pentafluoropropene as obtained by the method of claim 1 or 2 as the raw material with hydrogen in the vapor phase under the presence of a rhodium catalyst.

11. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to claim 10 wherein the rhodium catalyst is carried by at least one carrier of active carbon, alumina, silica gel, titanium oxide and zirconia.

12. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to claim 10 wherein the carrying concentration of the rhodium catalyst on the carrier is 0.05 weight% to 10 weight%.

13. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 10 to 12 wherein at least a stoichiometric amount of hydrogen to 1,1,1,2,3-pentafluoropropene is used.

14. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 10 to 13 wherein the reaction is conducted within a range of 30°C to 450°C.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 10 5492

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-2 461 523 (D.D. COFFMAN ET AL.) 15 February 1949 * claims * ---	1	C07C17/25 C07C17/354 C07C19/08 C07C21/18
D,A	DATABASE WPI Section Ch, Week 9026 Derwent Publications Ltd., London, GB; Class E16, AN 90-196843 XP002003320 & JP-A-02 129 131 (ASAHI GLASS KK) , 17 May 1990 * abstract * -----	3	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 May 1996	Bonnevalle, E

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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(71) Applicant: **DAIKIN INDUSTRIES, LIMITED**
Umeda Center Building, 4-12, Nakazaki-nishi 2-chome
Kita-ku
Osaka-shi
Osaka 530 (JP)

(72) Inventor: **AOYAMA, Hirokazu Yodogawa Woks of Daikin Ind. Ltd.**
1-1, Nishihitotsuya,
Settsu-shi,
Osaka 566
1-1,
Nishihitotsuya,
Settsu-sh (JP)
Inventor: **SEKI, Eiji Yodogawa Works of Daikin Ind.**
Ltd. 1-1,Nishihitotsuya
Settsu-shi,
Osaka 566 (JP)

(74) Representative: **ter Meer, Nicolaus, Dipl.-Chem., Dr. et al**
Patentanwälte
TER MEER-MÜLLER-STEINMEISTER & PARTNER
Mauerkircherstrasse 45
D-81679 München (DE)

(54) **PROCESSES FOR PRODUCING 1,1,1,2,3-PENTAFLUOROPROPENE AND PRODUCING 1,1,1,2,3-PENTAFLUOROPROPANE.**

(57) A process for producing 1,1,1,2,3-pentafluoropropene in a high yield from a readily available 1,1,1,2,3,3-hexafluoropropane industrially at a low cost, which process comprises bringing the gaseous hexafluoropropane into contact with active carbon optionally containing a metallic salt to effect dehydrofluorination. A process for producing 1,1,1,2,3-pentafluoropropane at a high conversion and a high selectivity, which comprises reducing 1,1,1,2,3-pentafluoropropene with hydrogen in the presence of either a hydrogenation catalyst comprising palladium and, added thereto, one or more metals selected from among silver, copper, gold, tellurium, zinc, chromium, molybdenum and thallium, or a rhodium catalyst.

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Fields of Industrial Application

The present inventions relate to methods for manufacturing 1,1,1,2,3-pentafluoropropene, which is useful as an intermediate for compounds that can be substitutes for CFC and HCFC as refrigerants, blowing agents and cleaning agents, and as a monomer of macromolecule compounds, and methods for manufacturing 1,1,1,2,3-pentafluoropropane, which is a useful compound that can be said substitutes for CFC and HCFC for said uses.

Conventional Methods

Among the conventionally known manufacturing methods of 1,1,1,2,3-pentafluoropropene are: 1) the method of 1,1,1,2,3,3-hexafluoropropane (which is produced by hydrogenating hexafluoropropene) being reacted with an aqueous solution of KOH with a 70% to 80% concentration at 150 °C (Ann. Chim. (Italy) vol. 55, 850p, 1965); and 2) the method of 1,1,1,2,3,3-hexafluoropropane being reacted with KOH in dibutylether (Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1412p, 1960). Another known method is: the method of removing HF from 1,1,1,2,3,3-hexafluoropropane by means of granular KCl in the gaseous phase at 700 °C to produce the desired product (Ann. Chim. (Italy) vol. 55, 850p, 1965).

Those methods, however, contained in the above-mentioned literature are not cost-effective because a large amount of alkali is used. As to the gaseous reaction process with KCl, it does not suit to the industrial production because it produces a 30% large amount of 1,1,1,3,3-pentafluoropropene having a boiling point approximate to that of 1,1,1,2,3-pentafluoropropene and being difficult to be separate by the ordinary rectification methods cannot well separate away.

The known manufacturing method of 1,1,1,2,3-pentafluoropropane is the method of hydrogenating 1,1,1,2,3-pentafluoropropene as a raw material (Izvest. Akad. Nauk S.S.S.R. 1960, 1412-18).

This method, however, has a low yield because it also further hydrogenates the material and produces 1,1,1,2-tetrafluoropropane. The method does not suit to the industrial production because 1,1,1,2-tetrafluoropropane, which is azeotropic or pseudo-azeotropic with 1,1,1,2,3-pentafluoropropane, is difficult to separate.

Objectives of the Inventions

An objective of the present inventions is to provide a highly cost-effective industrial method to produce 1,1,1,2,3-pentafluoropropene at high yields.

The other objective of those inventions is to provide a method with high reactivities and selectivities to produce 1,1,1,2,3-pentafluoropropane.

Contents of the Inventions

The inventors have thoroughly studied cost-effective industrial production methods of 1,1,1,2,3-pentafluoropropene, particularly those by means of the reaction to remove hydrogen fluroride from 1,1,1,2,3,3-hexafluoropropane which is obtained by hydrogenating hexafluoropropene, which is easily available. As a result, they have discovered that the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with active carbon causes a reaction of removing HF to produce 1,1,1,2,3-pentafluoropropene at high yields. The first invention has been achieved based on this discovery.

That is, the first invention relates to a method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the creation of reaction to remove HF from 1,1,1,2,3,3-hexafluoropropane by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with active carbon.

For the first invention, it is essential to make 1,1,1,2,3,3-hexafluoropropane in the gaseous state contact with active carbon. This is in practice a form of vapor phase reaction in which, for example, 1,1,1,2,3,3-hexafluoropropane in the gaseous state is made flow through a reaction tube filled with active carbon at a specific temperature. The methods of the vapor-phase reaction can be the fixed-bed reaction, the fluid-bed reaction and so on.

There are no particular restrictions in terms of kinds of active carbon to be used. A granular active carbon product, Shirasagi C, made by Takeda Yakuhin Kogyo Co., Ltd. and a coconut shell active carbon product, Yashicoal, made by Taihei Kagaku Sangyo Co., Ltd. can preferably be used.

The appropriate reaction temperature is 200 °C to 600 °C or more appropriately 250 °C to 500 °C . The above-stated reaction does progress very little under that temperature range and can produce a large amount of unfavorable by-products over that range.

The contact time with active carbon can be largely varied, but it is ordinarily 0.1 second to 200 seconds or more appropriately 0.5 second to 120 seconds.

There are various methods available to produce pentafluoropropane or 1,1,1,2,3-pentafluoropropane, which can be a substitute for CFC and HCFC, from 1,1,1,2,3-pentafluoropropene, which can be produced by means of the first invention.

An example of those methods is the hydrogenation reaction which is contained in Izvest. Akad. Nauk S.S.S.R., 1960, 1412-18. Another method to produce 1,1,1,2,3-pentafluoropropane with a higher yield is vapor-phase hydrogenation reaction with a palladium catalyst particularly at 30 °C to 450 °C.

The methods of said vapor-phase reaction can be the fixed-bed reaction, the fluid-bed reaction and so on.

The palladium catalyst is preferably carried by at least one selected from active carbon, alumina, silica gel, titanium oxide and zirconia, or other carrier.

The particle size of the carrier is preferably 0.1 mm to 100 mm although it has little effect on the reaction.

The acceptable range of the carrying concentration is from 0.05% to 10%, but the normally recommended range is 0.5% to 5% by weight.

The reaction temperature is ordinarily 30 °C to 450 °C or more appropriately 70 °C to 400 °C.

The ratio of hydrogen and the raw material in the 1,1,1,2,3-pentafluoropropene hydrogenation reaction can be largely varied. The reaction should, however, be ordinarily conducted with a stoichiometric amount of hydrogen with a minumum. An amount of hydrogen, such as 4 mol or more, which is far more than the stoichiometric one can be used for the whole mol of the starting material.

There are no restrictions on the reaction pressure so that the reaction can be conducted under a high pressure, a reduced pressure and the atmospheric pressure. It is preferable to conduct the reaction under a high pressure or the atmospheric pressure because the reduced pressure requires more complicated devices.

The contact time in the hydrogenation reaction is ordinarily 0.1 second to 300 seconds or more appropriately 1 second to 30 seconds.

The inventors have discovered that the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with active carbon added with metallic salt causes a reaction to remove HF to produce 1,1,1,2,3-pentafluoropropene at high yields. The second invention has been achieved based on this discovery.

That is, the second invention relates to a method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction to remove HF from 1,1,1,2,3,3-hexafluoropropane by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with active carbon added with metallic salt.

For the production method of the second invention, one or more kinds of metallic salt belonging to the element groups I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII, and XIV in accordance with the newly proposed periodic table by IUPAC in 1985 should be preferably added to active carbon to be used.

In this case, it is better to add at least one of metallic salts composed of potassium, silver, zinc, copper and magnesium to that active carbon for the above-mentioned use.

For the second invention, it is essential to make 1,1,1,2,3,3-hexafluoropropane in the gaseous state contact with active carbon added with the above-stated metallic salt. This is in practice a form of vapor phase reaction in which, for example, 1,1,1,2,3,3-hexafluoropropane in the gaseous state is made flow through a reaction tube filled with active carbon added with the metallic salt at a specific temperature. The methods of the vapor-phase reaction can be the fixed-bed reaction, the fluid-bed reaction and so on.

There are no particular restrictions in terms of kinds of active carbon to be used in the second invention. A granular active carbon product, Shirasagi C, made by Takeda Yakuhin Kogyo Co., Ltd. and coconut shell active carbon products, Yashicoal, made by Taihei Kagaku Sangyo Co., Ltd. and Kuraraycoal, made by Kuraray Chemical Co. Ltd. etc. can preferably be used.

The above-stated metallic salts should preferably include at least one of potassium chloride, potassium fluoride, silver nitrate, zinc chloride, magnesium chloride, and copper chloride (II) etc. The amount of metallic salt added to active carbon is acceptably 0.1 weight% to 50 weight% or more appropriately 0.5 weight% to 30 weight%.

The appropriate reaction temperature in the manufacturing method of the second invention is 200 °C to 600 °C or more appropriately 250 °C to 500 °C. The reaction does progress very little under 200 °C and is liable to produce a large amount of unfavorable dissolved by-products over 600 °C.

The contact time can be largely varied, but it is ordinarily 0.1 second to 300 seconds or more appropriately 0.5 second to 120 seconds.

The inventors have discovered that the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with active carbon which is treated with water or with active carbon under the presence of water causes a

reaction to remove HF to produce 1,1,1,2,3-pentafluoropropene at high yields. The third invention has been achieved based on this discovery.

That is, the third invention relates to a method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction to remove HF from 1,1,1,2,3,3-hexafluoropropane by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with active carbon which is treated with water or with active carbon under the presence of water.

For the third invention, it is essential to make 1,1,1,2,3,3-hexafluoropropane in the gaseous state contact with active carbon which is treated with water or with active carbon under the presence of water. This is in practice a form of vapor phase reaction in which, for example, 1,1,1,2,3,3-hexafluoropropane in the gaseous state is made flow through a reaction tube filled with active carbon treated with water at a specific temperature, or 1,1,1,2,3,3-hexafluoropropane in the gaseous state is made flow through over active carbon under the presence of water. The methods of the vapor-phase reaction can be the fixed-bed reaction, the fluid-bed reaction and so on.

There are no particular restrictions in terms of kinds of active carbon to be used. The above-stated products can preferably be used.

There are no particular restrictions in terms of the method of water treatment on active carbon. The water immersion of active carbon and the vapor-phase steam treatment are acceptable. For the reaction procedure of flowing 1,1,1,2,3,3-hexafluoropropane concurrently with water, the amount of water content in the reaction gas should be ordinarily 1 ppm to 10%, or preferably 10 ppm to 5%.

The appropriate reaction temperature and contact time are 200 °C to 600 °C (or more appropriately 250 °C to 500 °C) and 0.1 second to 300 seconds (or more appropriately 0.5 second to 120 seconds), respectively, as in the above.

The inventors have discovered that the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with trivalent chromium oxide or partly fluorinated trivalent chromium oxide causes a reaction to remove HF to produce 1,1,1,2,3-pentafluoropropene at high yields. The fourth invention has been achieved based on this discovery.

That is, the fourth invention relates to a method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction to remove HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with trivalent chromium oxide or partly fluorinated trivalent chromium oxide.

The inventors have discovered that the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with either chromium (III) oxides or partly fluorinated chromium (III) oxides under the presence of oxygen causes a reaction to remove HF to produce 1,1,1,2,3-pentafluoropropene at high yields, and that the catalyst for this process tends to retain activity longer and have a longer life. The fifth invention has been achieved based on this discovery.

That is, the fifth invention relates to a method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction to remove HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with either chromium (III) oxides or partly fluorinated chromium (III) oxides under the presence of oxygen.

For the fifth invention, it is essential to make 1,1,1,2,3,3-hexafluoropropane in the gaseous state contact with either chromium (III) oxides or partly fluorinated chromium (III) oxides under the presence of oxygen. This is in practice a form of vapor phase reaction in which, for example, 1,1,1,2,3,3-hexafluoropropane in the gaseous state is made flow through a reaction tube filled with either chromium (III) oxides or partly fluorinated chromium (III) oxides at a specific temperature. The methods of the vapor-phase reaction can be the fixed-bed reaction, the fluid-bed reaction and so on.

For this invention, any preparation method of a catalyst comprising chromium (III) oxides or partly fluorinated chromium (III) oxides is acceptable. Chromium oxide can, for example, be prepared by reducing CrO_3 or by obtaining precipitate from a salt of Cr^{3+}.

A catalyst in the state of hydrate should be dried at 120 °C to 300 °C and then calcinated ordinarily at 300 °C to 600 °C or preferably at 350 °C to 450 °C.

The treatment to fluorinate (or activate) a catalyst should be conducted ordinarily at 20 °C to 450 °C or preferably at 200 °C to 400 °C for the purpose. That fluorination can be conducted, for example, with hydrogen fluoride anhydride in the fluorination reaction system or by means of the heating treatment with fluorinated hydrocarbon. Partly fluorinated chromium (III) oxide can be obtained by heating a CrF_3 hydrate with oxygen.

The appropriate reaction temperature and contact time are 200 °C to 600 °C (or more appropriately 250 °C to 500 °C) and 0.1 second to 300 seconds (or more appropriately 0.5 second to 120 seconds), respectively, as in the above.

The concentration of oxygen present in said reaction of removing HF can be largely varied, but should ordinarily 0.005% to 20% of the total flow or preferably 0.01% to 10% of the total flow. An oxygen-containing mixed gas such as air can be used in the reaction process. In such a case, the gas concentration must comply with the above criterion figures for oxygen concentration.

The inventors have thoroughly studied production methods of 1,1,1,2,3-pentafluoropropane through vapor-phase catalytic reduction with a palladium catalyst, especially the methods that do not cause the problems mentioned in the above. As a result, they have discovered that hydrogenating 1,1,1,2,3-pentafluoropropene (particularly obtained through the reaction of removing HF caused by the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with active carbon as described in the above) as the raw material in the vapor or liquid phase under the presence of a palladium alloy catalyst at particularly 0 °C to 550 °C is an industrially easy manufacturing method of 1,1,1,2,3-pentafluoropropane with high yields to achieve the objective with high selectivity and high yields. The sixth invention has been achieved based on this discovery.

That is, the point of the sixth invention is in a method for manufacturing 1,1,1,2,3-pentafluoropropane characterized by the reduction of 1,1,1,2,3-pentafluoropropene with hydrogen under the presence of a hydrogenation catalyst consisting of palladium added with one or more metals selected from silver, copper, gold, tellurium, zinc, chromium, molybdenum, and thallium.

For the sixth invention, it is essential to add other metal(s) to palladium.

An alloy catalyst is generally considered to show the characteristics of the each constituent element according to its composition. For the invention, the amount of added metallic constituents to palladium should appropriately be 0.01 weight% to 500 weight%, or optimally 0.1 weight% to 300 weight% to take the advantage of the characteristics of palladium.

The acceptable amount of the carrying concentration of palladium alloy on various kinds of carriers is from 0.05% to 10%, but the recommended range is ordinarily 0.5% to 2%.

For the sixth invention, the appropriate carriers of palladium alloy catalysts are active carbon, alumina, silica gel, zirconia, titania, and so on.

The particle size of the carrier is preferably 0.1 mm to 100 mm although it has little effect on the reaction.

The ratio of hydrogen and the raw material in the 1,1,1,2,3-pentafluoropropene hydrogenation reaction can be largely varied. The reaction should, however, be ordinarily conducted with at least a stoichiometric amount of hydrogen. An amount of hydrogen, such as 4 mol or more, which is far more than the stoichiometric one can be used for the whole mol of the starting material.

The reaction should be conducted in the liquid or vapor phase. The methods of the vapor-phase reaction can be the fixed-bed reaction, the fluid-bed reaction and so on.

There are no restrictions on the reaction pressure so that the reaction can be conducted under a high pressure, a reduced pressure and the atmospheric pressure. It is preferable to conduct the reaction under a high pressure or the atmospheric pressure because the reduced pressure requires more complicated devices.

The appropriate reaction temperature is 0 °C to 550 °C, and 50 °C to 450 °C for the vapor phase reaction.

For the vapor phase reaction, the contact time is ordinarily 0.1 second to 300 seconds or more appropriately 1 second to 30 seconds.

The material 1,1,1,2,3-pentafluoropropene used as the raw material for the method of the sixth invention can be synthesized through various methods.

Among those methods are: 1) the method of 1,1,1,2,3,3-hexafluoropropene (which is produced by hydrogenating hexafluoropropene) being reacted with an aqueous solution of KOH with a 70% to 80% concentration at 150 °C (Ann. Chim. (Italy) vol. 55, 850p, 1965); and 2) the method of being reacted with KOH in dibutylether (Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1412p, 1960); and so on. Another method is: the method of removing HF with granular KCl in the vapor phase at 700 °C to product the desired product (Ann. Chim. (Italy) vol. 55, 850p. 1965).

As a cost-effective industrial manufacturing method with high yield, a reaction to remove HF from easily available 1,1,1,2,3,3-hexafluoropropane in the gaseous state by making contact with active carbon can be adopted.

Such methods for the vapor-phase reaction can be the fixed-bed reaction, the fluid-bed reaction and so on.

There are no particular restrictions in terms of kinds of active carbon to be used. A granular active carbon product, Shirasagi C, made by Takeda Yakuhin Kogyo Co., Ltd. and a coconut shell active carbon product, Yashicoal, made by Taihei Kagaku Sangyo Co., Ltd. can preferably be used.

The appropriate reaction temperature is 200 °C to 600 °C or more appropriately 250 °C to 500 °C. It is not preferable that the above-stated reaction does progress very little under that temperature range and can produce a large amount of unfavorable dissolution by-products over that range.

The contact time with active carbon can be largely varied, but it is ordinarily 0.1 second to 200 seconds or more appropriately 0.5 second to 120 seconds.

The inventors have thoroughly studied production methods of 1,1,1,2,3-pentafluoropropane to solve the problems mentioned in the above. As a result, they have discovered that hydrogenating 1,1,1,2,3-pentafluoropropene as the raw material in the vapor phase under the presence of a rhodium catalyst brings about obtaining the target product at high yields. The seventh invention has been achieved based on this discovery.

That is, the seventh invention relates to a method for manufacturing 1,1,1,2,3-pentafluoropropane especially at a 97% or more high yield by means of the hydrogenation reaction on 1,1,1,2,3-pentafluoropropene as the starting material under the presence of a rhodium catalyst especially at 30 °C to 450 °C.

For the seventh invention, it is essential to hydrogenate the material in the vapor phase by means of a rhodium catalyst. The methods of the vapor-phase reaction can be the fixed-bed reaction, the fluid-bed reaction and so on.

The rhodium catalysts are preferably supported on one or more carriers selected from active carbon, alumina, silica gel, titanium oxide, zirconia, and so on.

The particle size of the carrier is preferably 0.1 mm to 100 mm although it has little effect on the reaction.

The acceptable amount of the carrying concentration of rhodium is from 0.05 weight% to 10 weight%, but the recommended range is ordinarily 0.5 weight% to 5 weight%.

The appropriate reaction temperature is ordinarily 30 °C to 450 °C or more appropriately 70 °C to 250 °C.

For the seventh invention, the ratio of hydrogen and the raw material for the 1,1,1,2,3-pentafluoropropene hydrogenation reaction can be largely varied. The reaction should, however, be ordinarily conducted with at least a stoichiometric amount of hydrogen. An amount of hydrogen, such as 2 mol or more, which is far more than the stoichiometric, one can be used for the whole mol of the starting material.

There are no restrictions on the reaction pressure so that the reaction can be conducted under a high pressure, a reduced pressure and the atmospheric pressure. It is preferable to conduct the reaction under a high pressure or the atmospheric pressure because the reduced pressure requires more complicated devices.

The contact time is ordinarily 0.1 second to 300 seconds or more appropriately 1 second to 30 seconds.

Industrial Applicability

The present inventions make it possible to produce 1,1,1,2,3-pentafluoropropene, which is useful as an intermediate of useful compounds that can be substitutes for CFC and HCFC as refrigerants, blowing agents and cleaning agents, and as a monomer of macromolecule compounds from easily available 1,1,1,2,3,3-hexafluoropropane, by cost-effective industrial methods with high yields.

They also make it possible to produce 1,1,1,2,3-pentafluoropropane at high yields and high selectivities by reducing with hydrogen 1,1,1,2,3-pentafluoropropene under the presence of a rhodium catalyst or of a hydrogenation catalyst created by adding palladium with one or more metals selected from silver, copper, gold, tellurium, zinc, chromium, molybdenum, and thallium.

Embodiments

The inventions are more specifically explained with their embodiments hereunder.

Embodiment 1

20 cc of granular active carbon (Shirasagi C made by Takeda Yakuhin Kogyo Co., Ltd.) was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 430 °C while nitrogen gas was flowed through the tube. After 2 hours of the heating at that temperature, 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 20 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and

then dried with calcium chloride. Table 1 shows the results.

Embodiment 2

The similar procedures to those in Embodiment 1 was conducted with 20 cc of coconut shell active carbon (Yashicoal made by Taihei Kagaku Sangyo Co., Ltd.) filled in the same kind of reaction tube that was heated at 450 °C. Table 1 shows the results.

Table 1

	Embodiment 1	Embodiment 2
Conversion (%)	60.9	83.7
Selectivity of 1,1,1,2,3-pentafluoropropene * (%)	90.5	96.9

* Selectivity: % of the mixture of E and Z of 1,1,1,2,3-pentafluoropropene is shown.

The above results demonstrate that reaction according to the present inventions can produce the desired product on a cost-effective and high-yield basis.

Moreover, 20 cc of a palladium catalyst carried by alumina with a concentration of 0.5% was filled in an SUS316 reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 80 °C while nitrogen gas was flowed through it. After the tube was heated up to a given temperature, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized in advance, was introduced into the tube at 57 cc/min with hydrogen introduced at 114 cc/min. The reaction temperature was maintained at 80 °C. The produced gas (1,1,1,2,3-pentafluoropropane) was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. The results were excellent with 100% of reactivity and 99% of selectivity.

Embodiment 3

25 cc of aqueous solution containing 0.95 g of KCl added with 10 g of Yashicoal M was stirred for 4 hours at 50 °C. After water was distilled away under reduced pressure, it was dried at 120 °C for 24hours. The resulted 8 g of catalyst was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length. Then the tube was heated in a electric furnace at 450 °C while nitrogen gas was flowed through the tube. 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 24 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 2 shows the results.

Embodiment 4

25 cc of aqueous solution containing 0.74 g of KF added with 10 g of Yashicoal M was stirred for 4 hours at 50 °C. After water was distilled away under reduced pressure, it was dried for 24hours at 120 °C. The resulted 8 g of catalyst was filled into the same kind of reaction tube as Embodiment 3. The reaction was conducted by flowing 1,1,1,2,3,3-hexafluoropropane through the tube at 24 ml/min at a reaction temperature of 450 °C. Table 2 shows the results.

Embodiment 5

25 cc of aqueous solution containing 0.79 g of $AgNO_3$ added with 10 g of Yashicoal M was stirred for 4 hours at 50 °C. After water was distilled away under reduced pressure, it was dried for 24hours at 120 °C. The resulted 8 g of catalyst was filled into the same kind of reaction tube as Embodiment 3. The reaction was conducted by flowing 1,1,1,2,3,3-hexafluoropropane through the tube at 32 ml/min at a reaction temperature of 450 °C. Table 2 shows the results.

Embodiment 6

25 cc of aqueous solution containing 1.3 g of $CuCl_2$ added with 10 g of Yashicoal M was stirred for 4 hours at 50 °C. After water was distilled away under reduced pressure, it was dried for 24hours at 120 °C.

The resulted 8 g of catalyst was filled into the same kind of reaction tube as Embodiment 3. Then a similar operation was performed, that is, the reaction was conducted by flowing 1,1,1,2,3,3-hexafluoropropane through the tube at 32 cc/min at a reaction temperature of 450 °C. Table 2 shows the results.

Embodiment 7

25 cc of aqueous solution containing 1.95 g of $MgCl_2$ added with 10 g of Yashicoal M was stirred for 4 hours at 50 °C. After water was distilled away under reduced pressure, it was dried for 24hours at 120 °C. The resulted 8 g of catalyst was filled into the same kind of reaction tube as Embodiment 3. The reaction was conducted by flowing 1,1,1,2,3,3-hexafluoropropane through the tube at 24 cc/min at a reaction temperature of 450 °C. Table 2 shows the results.

Embodiment 8

8 g of Yashicoal M was filled in an SUS316 reaction tube of 2 cm inner diameter and 40 cm length. Then the tube was heated in an electric furnace at 400 °C while nitrogen gas was flowed through the tube.

Then 1,1,1,2,3,3-hexafluoropropane containing 4000 ppm of water was flowed through the tube at 24 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 3 shows the results.

Embodiment 9

8 g of Yashicoal M was filled in an SUS316 reaction tube of 2 cm inner diameter and 40 cm length. Then the tube was heated in an electric furnace at 300 °C while water steam was flowed at 50 cc/min through the tube for 2 hours.

Then 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 24 cc/min at 400 °C, replacing water steam. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 3 shows the results.

Embodiment 10

Chromium hydroxide prepared from an aqueous solution of chromium nitrate and aqueous ammonia was filtrated, washed with water, and dried at 100 °C. The resulted material was shaped into a cylinder of 3 mm inner diameter and 3 mm height by means of a tapping forming machine. The obtained catalyst was filled into a Hastelloy C reaction tube before the reaction and was activated by heating it at a constant temperature 400 °C in a nitrogen gas flow for 1 hour. Then, after the temperature was lowered down to 200 °C, the catalyst was fluorinated by treating it with a supply of hydrogen fluoride anhydride diluted with N_2 for 5 hours.

10 g of the prepared catalyst was filled into a Hastelloy C reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 350 °C while flowing nitrogen gas through it.

Then 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 30 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 4 shows the results.

Embodiment 11

10 g of the catalyst prepared according to the procedures in Embodiment 10 before the hydrogen fluoride anhydride treatment was filled into a Hastelloy C reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 400 °C while nitrogen gas was flowed through it.

Then 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 40 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 4 shows the results.

Embodiment 12

Chromium hydroxide prepared from an aqueous solution of chromium nitrate and aqueous ammonia was filtrated, washed with water, and dried at 100 °C. The resulted material was shaped into a cylinder of 3 mm diameter and 3 mm height by means of a tapping forming machine. The obtained catalyst was filled

into a Hastelloy C reaction tube before the reaction and was heated at a constant temperature 400 °C in a nitrogen gas flow for 1 hour. Then, after the temperature was lowered down to 200 °C, the catalyst was activated by treating it with a supply of hydrogen fluoride anhydride for 1 hours.

20 g of the prepared catalyst was filled into a Hastelloy C reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 350 °C while flowing nitrogen gas through it.

Then 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 57 cc/min with oxygen flowed at 3 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 5 shows the conversion rate and selectivity 1 hour after the start of the reaction and those 100 hours after that.

Embodiment 13

20 g of the catalyst prepared according to the procedures in Embodiment 12 was filled into a Hastelloy C reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 350 °C while nitrogen gas was flowed through it.

Then 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 54 cc/min with air flowed at 6 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 5 shows the conversion rate and selectivity 1 hour after the start of the reaction and those 100 hours after that.

Embodiment 14

20 g of the catalyst prepared according to the procedures in Embodiment 12 was filled into a Hastelloy C reaction tube of 2 cm inner diameter and 40 cm length and the tube was heated in an electric furnace at 350 °C while nitrogen gas was flowed through it.

Then 1,1,1,2,3,3-hexafluoropropane was flowed through the tube at 60 cc/min, replacing nitrogen gas. The gas from the tube outlet was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 5 shows the conversion rate and selectivity 1 hour after the start of the reaction and those 100 hours after that.

Table 2

	Conversion (%)	Selectivity * (%)
Embodiment 3	79.5	98.2
Embodiment 4	85.7	97.5
Embodiment 5	70.5	96.9
Embodiment 6	65.5	97.0
Embodiment 7	68.7	97.0

* Selectivity: % of the mixture of E and Z of 1,1,1,2,3-pentafluoropropene is shown. (The same applies hereinafter.)

Table 3

	Conversion (%)	Selectivity (%)
Embodiment 8	75.2	97.8
Embodiment 9	75.0	97.5

Table 4

	Conversion (%)	Selectivity (%)
Embodiment 10	95.1	99.3
Embodiment 11	90.0	99.2

Table 5

	1 hour after the reaction started		100 hours after the reaction started	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
Embodiment 12	85.4	99.7	85.1	99.6
Embodiment 13	85.3	99.8	85.1	99.6
Embodiment 14	85.1	99.8	45.2	99.5

The results of the embodiments described above clearly demonstrate that 1,1,1,2,3-pentafluoropropene is obtained from easily available 1,1,1,2,3,3-hexafluoropropane by a cost-effective industrial method with high yields in accordance with the present inventions.

Embodiment 15

Palladium catalyst carried by active carbon at a 0.5% concentration was added to an aqueous solution of $CuCl_2$ of 0.1% concentration as Cu to the active carbon and was dropped with 0.2 ml of formalin. After the resulted substance was heated at 50 °C for 5 hours, it was distilled to remove water under reduced pressure and then it was dried for 24hours at 100 °C.

18 cc of the obtained catalyst was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length, and the tube was heated in an electric furnace at 350 °C for 3 hours while hydrogen gas was flowed through it at 40 cc/min. Then, after the temperature was lowered down to an appropriate level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced into the tube at 20 cc/min with hydrogen introduced at 40 cc/min. The reaction temperature was 80 °C. This 1,1,1,2,3-pentafluoropropene was that which was made in Embodiment 2.

The produced gas, which contains 1,1,1,2,3-pentafluoropropane, was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 6 shows the results.

Embodiment 16

Palladium catalyst carried by active carbon at a 0.5% concentration was added with silver by the use of $AgNO_3$ at a 0.1% concentration as Ag to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 15. Then the same reaction as Embodiment 15 was conducted. Table 6 shows the results.

Embodiment 17

Palladium catalyst carried by active carbon at a 0.5% concentration was added with tellurium by the use of $TeCl_2$ at a 0.1% concentration as Te to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 15. Then the same reaction as Embodiment 15 was conducted. Table 6 shows the results.

Embodiment 18

Palladium catalyst carried by active carbon at a 0.5% concentration was added with gold by the use of $AuCl_3$ at a 0.1% concentration as Au to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 15. Then the same reaction as Embodiment 15 was conducted. Table

6 shows the results.

Embodiment 19

Palladium catalyst carried by active carbon at a 0.5% concentration was added with zinc by the use of $ZnCl_2$ at a 2% concentration as Zn to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 15. The obtained alloy catalyst was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length, and the tube was heated in an electric furnace at 350 °C while hydrogen gas was flowed through it at 40 cc/min.

Then, after the temperature was lowered down to a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced into the tube at 40 cc/min with hydrogen introduced at 80 cc/min. The reaction temperature was 100 °C.

The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 6 shows the results.

Embodiment 20

Palladium catalyst carried by active carbon at a 0.5% concentration was added with chromium by the use of $Cr(NO_3)_3 \cdot 9H_2O$ at a 2% concentration as Cr to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 15. 17cc of the obtained alloy catalyst was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length, and the tube was heated in an electric furnace at 400 °C while hydrogen gas was flowed through it.

Then, after the temperature was lowered down to a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced into the tube at 30 cc/min with hydrogen introduced at 60 cc/min. The reaction temperature was 100 °C.

The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 6 shows the results.

Embodiment 21

Palladium catalyst carried by active carbon at a 0.5% concentration was added with thallium by the use of $TlCl_3$ at a 2% concentration as Tl to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 15. 15cc of the obtained alloy catalyst was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length, and the tube was heated in an electric furnace at 350 °C while hydrogen gas was flowed through it at 40 cc/min.

Then, after the temperature was lowered down to a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced into the tube at 40 cc/min with hydrogen introduced at 80 cc/min. The reaction temperature was 150 °C.

The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 6 shows the results.

Embodiment 22

Palladium catalyst carried by active carbon at a 0.5% concentration was added with molybdenum by the use of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ at a 2% concentration as Mo to prepare an alloy catalyst in accordance with the preparation procedures described in Embodiment 15. 15 cc of the obtained alloy catalyst was filled into an SUS316 reaction tube of 2 cm inner diameter and 40 cm length, and the tube was heated in an electric furnace at 350 °C while hydrogen gas was flowed through it at 40 cc/min.

Then, after the temperature was lowered down to a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced into the tube at 30 cc/min with hydrogen introduced at 60 cc/min. The reaction temperature was 120 °C.

The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 6 shows the results.

Embodiment 23

Palladium catalyst carried by powdered active carbon at a 5% concentration was added with an aqueous solution of $AgNO_3$ of 1% concentration against the active carbon and then was added with 0.2 ml

of formalin. After the resulted substance was heated for 5 hours at 50 °C, it was distilled to remove water under reduced pressure. Analysis showed that the obtained catalyst contained 54% of water.

1 g of the obtained catalyst was put in an SUS316 autoclave of 200 cc. After the nitrogen substitution, 10 g of 1,1,1,2,3-pentafluoropropene was introduced into the autoclave. Then hydrogen gas was introduced until its amount reaches 9 kg/cm^2 at a room temperature while stirring. Hydrogen gas was added each time it was consumed and the reaction was maintained until hydrogen gas was not consumed any more. The reaction temperature was held at 25 °C or under.

After the reaction finished, the reaction liquid was analyzed by gas chromatography. Table 6 shows the results.

Table 6

Embodiment No.	Conversion (%)	Selectivity (%)
15	99	98
16	99	98
17	99	96
18	99	98
19	98	97
20	99	97
21	98	96
22	98	96
23	99	98

The above results demonstrate that hydrogenation reaction according to the present inventions can produce the desired product at high conversion and high selectivity.

Embodiment 24

10 cc of a rhodium catalyst carried by alumina at 0.5% concentration was filled in an SUS316 reaction tube of 2 cm inner diameter and 40 cm length. Then the tube was heated in an electric furnace at 80 °C while nitrogen gas was flowed through the tube.

After the tube temperature reached a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced at 26.7 cc/min with hydrogen introduced at 55.3 cc/min. The reaction temperature was held at 80 °C. The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 7 shows the results.

Embodiment 25

18 cc of a rhodium catalyst carried by active carbon at 0.5% concentration was filled into the same reaction device as Embodiment 24. Then the device was heated in an electric furnace at 120 °C while nitrogen gas was flowed through the tube.

After the tube temperature reached a specific level, gaseous 1,1,1,2,3-pentafluoropropene, which had been vaporized, was introduced at 40 cc/min with hydrogen introduced at 80 cc/min. The reaction temperature was held at 120 °C. The produced gas was analyzed by gas chromatography after being washed with water and then dried with calcium chloride. Table 7 shows the results.

Table 7

Embodiment No.	Conversion (%)	Selectivity (%)
24	100	99
25	100	99

The above results demonstrate that reaction according to the present inventions can produce the desired product 1,1,1,2,3-pentafluoropropane at high yields.

Claims

1. A method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction of removing HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with active carbon.

2. A method for manufacturing 1,1,1,2,3-pentafluoropropene according to claim 1 wherein the reaction is conducted at 200 °C to 600 °C.

3. A method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction of removing HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with active carbon added with metallic salt.

4. A method for manufacturing 1,1,1,2,3-pentafluoropropene according to claim 3 wherein the active carbon is added with one or more kinds of salt of metal belonging to the element groups I, II, III, IV, V, VI, VII, VIII, IX, X, XI, XII, XIII, and XIV.

5. A method for manufacturing 1,1,1,2,3-pentafluoropropene according to claim 4 wherein the active carbon is added with salt of metal composed of one or more of potassium, silver, zinc, copper and magnesium.

6. A method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction of removing HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with active carbon treated with water or with active carbon under the presence of water.

7. A method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction of removing HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with trivalent chromium oxide or partly fluorinated trivalent chromium oxide.

8. A method for manufacturing 1,1,1,2,3-pentafluoropropene characterized by the reaction of removing HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with trivalent chromium oxide or partly fluorinated trivalent chromium oxide under the presence of oxygen.

9. A method for manufacturing 1,1,1,2,3-pentafluoropropane characterized by the reaction of the reduction of 1,1,1,2,3-pentafluoropropene with hydrogen under the presence of a hydrogenation catalyst consisting of palladium added with one or more of metal selected from silver, copper, gold, tellurium, zinc, chromium, molybdenum, and thallium.

10. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to claim 9 wherein at least a stoichiometric amount of hydrogen to 1,1,1,2,3-pentafluoropropene is used.

11. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to claim 9 or 10 wherein the reaction is conducted at 0 °C to 550 °C.

12. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 9, 10 and 11 wherein an alloy catalyst with a 0.01 weight% to 500 weight% concentration of an added metal constituent against the palladium concentration is used.

13. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 9, 10, 11 and 12 wherein a hydrogenation catalyst is used which is a catalyst consisting of palladium added with one or more of silver, copper, gold, tellurium, zinc, chromium, molybdenum and thallium and being carried by active carbon carrier.

14. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 9, 10, 11, 12 and 13 wherein a hydrogenation catalyst is used which is a catalyst consisting of palladium added with one or more of silver, copper, gold, tellurium, zinc, chromium, molybdenum and thallium and being carried by at least one carrier of active carbon, alumina, silica gel, titanium oxide and zirconia.

15. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 9, 10, 11, 12, 13 and 14 wherein the carrying concentration of a palladium alloy catalyst on the carrier is 0.05% to 10%.

16. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 9, 10, 11, 12, 13, 14 and 15 wherein 1,1,1,2,3-pentafluoropropene obtained by removing HF by means of the contact of 1,1,1,2,3,3-hexafluoropropane in the gaseous state with active carbon is used.

17. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to claim 16 wherein the reaction is conducted at 200 °C to 600 °C.

18. A method for manufacturing 1,1,1,2,3-pentafluoropropane characterized by the reaction of 1,1,1,2,3-pentafluoropropene as the raw material with hydrogen in the vapor phase under the presence of a rhodium catalyst.

19. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to claim 18 wherein the rhodium catalyst is carried by at least one carrier of active carbon, alumina, silica gel, titanium oxide and zirconia.

20. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to claim 19 wherein the carrying concentration of the rhodium catalyst on the carrier is 0.05 weight% to 10 weight%.

21. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 18, 19 and 20 wherein at least a stoichiometric amount of hydrogen to 1,1,1,2,3-pentafluoropropene is used.

22. A method for manufacturing 1,1,1,2,3-pentafluoropropane according to one of claims 18, 19, 20 and 21 wherein the reaction is conducted within a range of 30 °C to 450 °C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/00661

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl^5 C07C21/18, 17/34, 19/08, 17/00, B01J21/18, 21/10, 23/04, 23/06, 23/50, B01J23/72, 23/26, 23/52, 23/60, 23/62, 23/64, 23/89, 27/057, 23/46
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) Int. Cl^5 C07C21/18, 17/34, 19/08, 17/00, B01J21/18, 21/10, 23/04, 23/06, 23/50, B01J23/72, 23/26, 23/52, 23/60, 23/62, 23/64, 23/89, 27/057, 23/46

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)
CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3432562 (Phillips Petroleum Company), March 11, 1969 (11. 03. 69), (Family: none)	1-8, 16
A	JP, A, 54-130507 (Daikin Industries, Ltd.), October 9, 1979 (09. 10. 79), (Family: none)	7, 8
A	JP, A, 2-129131 (Asahi Glass Co., Ltd.), May 17, 1990 (17. 05. 90), (Family: none)	9-22

[X] 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 document but published on or after the international filing date
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
August 6, 1993 (06. 08. 93)	August 31, 1993 (31. 08. 93)
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(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for Preparing 1,1,1,4,4,4-Hexafluorobutane in the Liquid Phase

(72) Bielefeldt, Dietmar - Germany (Federal Republic of) ;
Lui, Norbert - Germany (Federal Republic of) ;
Marhold, Albrecht - Germany (Federal Republic of) ;

(71) Bayer Aktiengesellschaft - Germany (Federal Republic of) ;

(30) (DE) P 4421702.1 1994/06/21

(57) 8 Claims

Notice: This application is as filed and may therefore contain an incomplete specification.

Process for preparing 1,1,1,4,4,4-hexafluorobutane in the liquid phase

Abstract

1,1,1,4,4,4-Hexafluorobutane (R 356) can be obtained in a simple manner and in excellent yields and with excellent selectivities when 1,1,1,4,4,4-hexafluorobutene is reacted in the liquid phase with hydrogen in the presence of a noble metal catalyst.

BAYER AKTIENGESELLSCHAFT **51368 Leverkusen**

Konzernzentrale RP

Patente Konzern **Gai/klu/649-PE**

Process for preparing 1,1,1,4,4,4-hexafluorobutane in the liquid phase.

The present invention relates to a particularly selective process for preparing 1,1,1,4,4,4-hexafluorobutane (R 356) from 1,1,1,4,4,4-hexafluorobutene by hydrogenation.

It is already known that R 356 can be prepared by liquid-phase hydrogenation of chlorine-containing hexafluorobutenes or chlorine-free hexafluorobutine (see Y. Huang et al., Youji Huaxve 2 125 (1984) and DE-A 3 735 467, which corresponds to US-A 4 902 839). Chlorine-containing hexafluorobutenes here give hydrogen chloride which has to be removed as salt with the aid of a base. The removal of the salt and its further disposition requires special effort. In addition, the reaction product always still contains a considerable proportion of chlorine-containing products.

A disadvantage of the use of hexafluorobutine is that it is difficult and costly to obtain.

Furthermore, a liquid-phase process is known in which, likewise starting from hexafluorobutine, R 356 is obtained (J.A.C.S. 71 298 (1949)). Besides the fact that hexafluorobutine is difficult to obtain, it is a disadvantage that here R 356 is only obtained in yields of at most 27% of theory.

There is thus still the need for a process by means of which R 356 can be obtained from readily available starting materials in good yields and without disposal of byproducts.

A process has now been found for preparing 1,1,1,4,4,4,-hexafluorobutane (R 356) which is characterized in that 1,1,1,4,4,4-hexafluorobutene is reacted in the liquid phase with hydrogen in the presence of a noble metal catalyst.

1,1,1,4,4,4-Hexafluorobutene is readily obtainable from 1,1,1,4,4-pentafluoro-3,4-dichlorobutane by simultaneous fluorination and elimination.

The process of the invention is carried out at such combinations of pressure and temperature that the reaction mixture (with the exception of the catalyst) is essentially present in the liquid phase. Within this proviso, the pressure can be varied, for example, within the range from 0.5 to 300 bar and the temperature can be varied, for example, within the range from 0 to 250C. Since 1,1,1,4,4,4-hexafluorobutene boils at 9C at atmospheric pressure and 1,1,1,4,4,4-hexafluorobutane boils at 25C at atmospheric pressure, the reaction is frequently carried out at elevated pressure. Preference is given to temperatures in the range from 20 to 120C and pressures in the range from 2 to 100 bar.

The process of the invention can optionally be carried out in the presence of solvents. Examples of solvents which can be used here are alcohols, ethers and hydrocarbons. Preferably, however, no solvents are added.

The molar ratio of hydrogen to 1,1,1,4,4,4-hexafluorobutene used can be, for example, from 100 to 1:1. It is preferably in the range from 10 to 2:1.

The noble metal catalyst can be, for example, noble metals and/or noble metal compounds of transition groups VII and/or VIII of the Periodic Table of the Elements. These can optionally be arranged on a support, for example on silica, aluminium oxide, spinels, silicates or carbons. Suitable noble metal compounds are, in particular, oxides, hydroxides and hydrated oxides. Preference is given to noble metals and noble metal compounds of transition group VIII of the Periodic Table of the Elements, in particular metallic palladium on one of the specified support materials. Based on 1,1,1,4,4,4-hexafluorobutene, use can be made, for example, of

from 0.001 to 5% by weight of catalyst (calculated as metal). This amount is preferably from 0.05 to 1% by weight.

The process of the invention can be carried out continuously or batchwise. It can be carried out batchwise, for example, in a pressure vessel. After the reaction is complete, excess hydrogen can be separated from other constituents of the reaction mixture by decompression and can optionally be re-used. The catalyst can, for example, be separated off by filtration (optionally under pressure) or by vaporization of the vaporizable components of the reaction mixture (= virtually pure 1,1,1,4,4,4-hexafluorobutane). In this way, 1,1,1,4,4,4-hexafluorobutane is generally obtained in purities and yields of above 95%, frequently in purities above 99% and almost quantitative yields.

In the continuous mode of operation, the reaction can be carried out, for example, in one or more reactors connected in series, for example a cascade reactor, which contain the catalyst and to which 1,1,1,4,4,4-hexafluorobutene and hydrogen are fed and from which volatile components of the reaction mixture are taken. The catalyst can remain in the reactors, the excess hydrogen can be separated off by decompression and circulated. 1,1,1,4,4,4-Hexafluorobutane is then obtained in purities and yields as in the batchwise procedure.

A suitable material for the reaction vessels is, for example, stainless steel. It is generally advantageous to condition reaction vessels of stainless steel prior to their being used, for example by treatment with nitric acid.

In both cases (continuous and batchwise operation), the heat of reaction can be utilized to vaporize the product from the catalyst. A further purification of the 1,1,1,-4,4,4-hexafluorobutane thus prepared and isolated is generally not necessary.

The process of the invention has a series of advantages; virtually no byproducts which need to be disposed of, such as hydrogen chloride or salts, are formed, it starts out from readily available starting materials, it gives a 1,1,1,4,4,4-hexafluorobutane (R 356) in excellent yields and with excellent selectivities, the reaction mixture can

be worked up in a simple manner since virtually only excess hydrogen and the catalyst have to be removed from the product, and it requires no added materials such as bases.

Examples

Example 1

In a 20 l stainless steel autoclave, which had previously been conditioned using 10% strength nitric acid and was equipped with closed circuit heating and an anchor stirrer, 10.0 kg of 1,1,1,4,4,4-hexafluorobutene were heated from 0 to 30C over a period of 10 minutes in the presence of 250 g of catalyst (5% by weight of metallic palladium on activated carbon) at a pressure of 20 bar of hydrogen. After reaching this temperature, the hydrogen consumption was compensated for by repeated pressurization with fresh hydrogen at pressures between 20 and 30 bar. After about 2.5 hours the conversion was 87%. 1,1,1,4,4,4-Hexafluorobutane had been formed in a yield of greater than 99% of theory.

Example 2

The procedure was similar to Example 1, but the hydrogenation was carried out at 50C and after hydrogen uptake was complete the mixture was stirred for a further 3 hours at 50C. 1,1,1,4,4,4-Hexafluorobutane was then separated from the catalyst by pressure filtration. At a conversion of above 99.8%, 1,1,1,4,4,4-hexafluorobutane was obtained virtually quantitatively.

Example 3

The procedure was similar to that in Example 1, but the hydrogenation was carried out at 70C and at pressures of from 40 to 60 bar of hydrogen. After hydrogen uptake was complete, the mixture was stirred for a further 1 hour at 70C. 1,1,1,4,4,4-Hexafluorobutane was then separated from the catalyst by pressure filtration. The 1,1,1,4,4,4-hexafluorobutene had been converted virtually quantitatively.

WHAT IS CLAIMED IS:

1. A process for preparing 1,1,1,4,4,4-hexafluorobutane (R 356), in which 1,1,1,4,4,4-hexafluorobutene is reacted in the liquid phase with hydrogen in the presence of a noble metal catalyst.

2. The process of Claim 1, which is carried out at such combinations of pressure and temperature that the reaction mixture is essentially present in the liquid phase at pressures in the range from 0.5 to 300 bar and at temperatures in the range from 0 to 250C.

3. The process of Claim 1, in which the molar ratio of hydrogen to 1,1,1,4,4,4-hexafluorobutene used is from 100 to 1:1.

4. The process of Claim 1, in which the noble metal catalyst is selected from the group consisting of noble metals and noble metal compounds of transition group VII and/or VIII of the Periodic Table of the Elements.

5. The process of Claim 1, in which the noble metal catalyst is arranged on a support.

6. The process of Claim 1, in which from 0.001 to 5% by weight of noble metal catalyst (calculated as metal) is used.

7. The process of Claim 1, which is carried out continuously.

8. The process of Claim 1, which is carried out batchwise.

Fetherstonhaugh & Co.,
Ottawa, Canada
Patent Agents

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(71) Anmelder: BAYER AG
D-51368 Leverkusen (DE)

(72) Erfinder: Bielefeldt, Dietmar, Dr.
Southener Strasse 13
D-40883 Ratingen (DE)
Erfinder: Lui, Norbert, Dr.
Roggendorfstrasse 55
D-51061 Köln (DE)
Erfinder: Marhold, Albrecht, Dr.
Carl-Duisberg-Strasse 329
D-51373 Leverkusen (DE)

(54) **Herstellung von 1,1,1,4,4,4-Hexafluorbutan durch Umsetzung von 1,1,1,4,4,4-Hexafluorbuten mit Wasserstoff in Gegenwort eines Edelmetallkatalysators**

(57) Auf einfache Weise und in ausgezeichneten Ausbeuten und Selektivitäten kann man 1,1,1,4,4,4-Hexafluorbutan (R 356) erhalten, wenn man in flüssiger Phase 1,1,1,4,4,4-Hexafluorbuten mit Wasserstoff in Gegenwart eines Edelmetallkatalysators umsetzt.

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Die vorliegende Erfindung betrifft ein besonders selektives Verfahren zur Herstellung von 1,1,1,4,4,4-Hexafluorbutan (R 356) aus 1,1,1,4,4,4-Hexafluorbuten durch Hydrierung.

Es ist bereits bekannt R 356 durch Sumpfphasenhydrierung von Chlor enthaltenden Hexafluorbutenen oder chlorfreiem Hexafluorbutin herzustellen (siehe Y.Huang et al., Youji Huaxve 2 125 (1984) und DE-A 3 735 467, die der US-A 4 902 839 entspricht). Aus Chlor enthaltenden Hexafluorbutenen entsteht dabei Chlorwasserstoff, der mit Hilfe einer Base als Salz entfernt werden muß. Die Abtrennung des Salzes und dessen weiterer Verbleib erfordert besonderen Aufwand. Außerdem enthält das Reaktionsprodukt immer noch einen erheblichen Anteil Chlor enthaltender Produkte.

Nachteilig beim Einsatz von Hexafluorbutin ist dessen schwierige und kostspielige Zugänglichkeit.

Weiterhin ist ein Sumpfphasenverfahren bekannt, bei dem ebenfalls ausgehend von Hexafluorbutin R 356 erhalten wird (J. A. C. S. 71 298 (1949)). Neben der schwierigen Zugänglichkeit von Hexafluorbutin ist nachteilig, daß dabei R 356 nur in Ausbeuten von maximal 27 % der Theorie erhalten wird.

Es besteht also noch das Bedürfnis nach einem Verfahren mit dem R 356 aus gut zugänglichen Ausgangsmaterialien, in guten Ausbeuten und ohne Entsorgung von Nebenprodukten erhalten werden kann.

Es wurde nun ein Verfahren zur Herstellung von 1,1,1,4,4,4-Hexafluorbutan (R 356) gefunden, das dadurch gekennzeichnet ist, daß man in flüssiger Phase 1,1,1,4,4,4-Hexafluorbuten mit Wasserstoff in Gegenwart eines Edelmetallkatalysators umsetzt.

1,1,1,4,4,4-Hexafluorbuten ist aus 1,1,1,4,4-Pentafluor-3,4-dichlorbutan durch gleichzeitige Fluorierung und Eliminierung gut zugänglich.

Man führt das erfindungsgemäße Verfahren bei solchen Kombinationen von Druck und Temperatur durch, daß das Reaktionsgemisch (mit Ausnahme des Katalysators) im wesentlichen in flüssiger Phase vorliegt. Innerhalb dieser Vorgabe kann der Druck beispielsweise im Bereich von 0,5 bis 300 bar und die Temperatur beispielsweise im Bereich von 0 bis 250 °C variiert werden. Da 1,1,1,4,4,4-Hexafluorbuten bei Normaldruck bei 9 °C und 1,1,1,4,4,4-Hexafluorbutan bei Normaldruck bei 25 °C siedet, wird häufig bei erhöhtem Druck gearbeitet. Bevorzugt sind Temperaturen im Bereich von 20 bis 120 °C und Drucke im Bereich von 2 bis 100 bar.

Man kann das erfindungsgemäße Verfahren gegebenenfalls in Gegenwart von Lösungsmitteln durchführen. Beispielsweise kommen hier Alkohole, Ether und Kohlenwasserstoffe in Frage. Vorzugsweise setzt man aber keine Lösungsmittel zu.

Das Molverhältnis von Wasserstoff zu eingesetztem 1,1,1,4,4,4-Hexafluorbuten kann beispielsweise 100 bis 1:1 betragen. Vorzugsweise liegt es im Bereich von 10 bis 2 :1.

Bei dem Edelmetallkatalysator kann es sich z.B. um Edelmetalle und/oder Edelmetallverbindungen der VII. und/oder VIII. Nebengruppe des periodischen Systems der Elemente handeln. Diese können gegebenenfalls auf einem Träger angeordnet sein, beispielsweise auf Kieselsäure, Aluminiumoxid, Spinellen, Silikaten oder Kohlen. Als Edelmetallverbindungen kommen insbesondere Oxide, Hydroxide und Oxidhydrate in Frage. Bevorzugt sind Edelmetalle und Edelmetallverbindungen der VIII. Nebengruppe des Periodensystems der Elemente, insbesondere metallisches Palladium auf einem der genannten Trägermaterialien.

Bezogen auf 1,1,1,4,4,4-Hexafluorbuten kann man beispielsweise 0,001 bis 5 Gew.-% Katalysator (gerechnet als Metall) einsetzen. Vorzugsweise beträgt diese Menge 0,05 bis 1 Gew.-%.

Das erfindungsgemäße Verfahren kann kontinuierlich oder diskontinuierlich durchgeführt werden. Diskontinuierlich kann z.B. in einem Druckgefäß gearbeitet werden. Nach Beendigung der Reaktion kann man dabei durch Entspannen überschüssigen Wasserstoff von sonstigen Bestandteilen des Reaktionsgemisches abtrennen und gegebenenfalls wieder verwenden. Den Katalysator kann man z.B. durch Filtration (gegebenenfalls unter Druck) oder durch Abdampfung der verdampfbaren Anteile des Reaktionsgemisches (= praktisch reines 1,1,1,4,4,4-Hexafluorbutan) abtrennen. Man erhält so im allgemeinen 1,1,1,4,4,4-Hexafluorbutan in Reinheiten und Ausbeuten von über 95 %, häufig in Reinheiten über 99 % und nahezu quantitativen Ausbeuten.

Bei kontinuierlicher Arbeitsweise kann man z.B. in einem oder mehreren, hintereinandergeschalteten Reaktoren arbeiten, beispielsweise einem Kaskaden-Reaktor, die den Katalysator enthalten und denen 1,1,1,4,4,4-Hexafluorbuten und Wasserstoff zugeführt und verdampfbare Anteile des Reaktionsgemisches entnommen werden. Der Katalysator kann in den Reaktoren verbleiben, der überschüssige Wasserstoff kann durch Entspannung abgetrennt und im Kreis geführt werden. Es wird dann 1,1,1,4,4,4-Hexafluorbutan in Reinheiten und Ausbeuten wie bei der diskontinuierlichen Fahrweise erhalten.

Als Material für die Reaktionsgefäße kommt beispielsweise Edelstahl in Frage. Es ist im allgemeinen vorteilhaft, Reaktionsgefäße aus Edelstahl vor der Inbetriebnahme zu konditionieren, beispielsweise durch eine Behandlung mit Salpetersäure.

Man kann die Reaktionswärme in beiden Fällen (konti- und diskonti-Arbeitsweise) dazu benutzen,

um das Produkt vom Katalysator abzudampfen. Eine weitere Reinigung des so hergestellten und isolierten 1,1,1,4,4,4-Hexafluorbutans ist im allgemeinen nicht erforderlich.

Das erfindungsgemäße Verfahren hat eine Reihe von Vorteilen: Es entstehen praktisch keine zu entsorgenden Nebenprodukte wie Chlorwasserstoff oder Salze, es geht von gut zugänglichem Ausgangsmaterial aus; es liefert 1,1,1,4,4,4-Hexafluorbutan (R 356) mit ausgezeichneten Ausbeuten und Selektivitäten, das Reaktionsgemisch kann auf einfache Weise aufgearbeitet werden, da praktisch nur überschüssiger Wasserstoff und der Katalysator vom Produkt abzutrennen sind, und es benötigt keine Zusatzstoffe wie Basen.

Beispiele

Beispiel 1

In einem zuvor mit 10 %iger Salpetersäure konditionierten 20-l-Edelstahlautoklaven, der mit einer Umlaufheizung und einem Ankerrührer ausgerüstet war, wurden 10,0 kg 1,1,1,4,4,4-Hexafluorbuten in Gegewart von 250 g Katalysator (5 Gew.-% metallisches Palladium auf Aktivkohle) bei einem Druck von 20 bar Wasserstoff innerhalb von 10 Minuten von 0 auf 30 °C erwärmt. Nach dem Erreichen dieser Temperatur wurde der Wasserstoffverbrauch ausgeglichen durch mehrmaliges Aufdrükken von frischem Wasserstoff bei Drucken zwischen 20 und 30 bar. Nach ca. 2,5 Stunden lag der Umsatz bei 87 %. 1,1,1,4,4,4-Hexafluorbutan hatte sich in einer Ausbeute von größer als 99 % der Theorie gebildet.

Beispiel 2

Es wurde verfahren wie in Beispiel 1, jedoch wurde die Hydrierung bei 50 °C durchgeführt und nach Beendigung der Wasserstoffaufnahme noch 3 Stunden bei 50 °C nachgerührt. Danach wurde 1,1,1,4,4,4-Hexafluorbutan durch Druckfiltration vom Katalysator abgetrennt. Bei einem Umsatz von über 99,8 % wurde 1,1,1,4,4,4-Hexafluorbutan praktisch quantitativ erhalten.

Beispiel 3

Es wurde verfahren wie in Beispiel 1, jedoch wurde die Hydrierung bei 70 °C und bei Drucken von 40 bis 60 bar Wasserstoff durchgeführt. Nach Beendigung der Wasserstoffaufnahme wurde noch 1 Stunde bei 70 °C nachgerührt. Danach wurde 1,1,1,4,4,4-Hexafluorbutan durch Druckfiltrafion vom Katalysator abgetrennt. Das 1,1,1,4,4,4-Hexafluorbuten hatte sich praktisch quantitativ umgesetzt.

Patentansprüche

1. Verfahren zur Herstellung von 1,1,1,4,4,4-Hexafluorbutan (R 356), dadurch gekennzeichnet, daß man in flüssiger Phase 1,1,1,4,4,4-Hexafluorbuten mit Wasserstoff in Gegenwart eines Edelmetallkatalysators umsetzt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man es bei solchen Kombinationen von Druck und Temperatur durchführt, daß das Reaktionsgemisch bei Drucken im Bereich 0,5 bis 300 bar und Temperaturen im Bereich 0 bis 250 °C im wesentlich in flüssiger Phase vorliegt.

3. Verfahren nach Ansprüchen 1 bis 2, dadurch gekennzeichnet, daß das Molverhältnis von Wasserstoff zu eingesetztem 1,1,1,4,4,4-Hexafluorbuten 100 bis 1:1 beträgt.

4. Verfahren nach Ansprüchen 1 bis 3, dadurch gekennzeichnet, daß es sich bei dem Edelmetallkatalysator um Edelmetalle und/oder Edelmetallverbindungen der VII. und/oder VIII. Nebengruppe des Periodensystems der Elemente handelt.

5. Verfahren nach Ansprüchen 1 bis 4, dadurch gekennzeichnet, daß die Edelmetallkatalysatoren auf einem Träger angeordnet sind.

6. Verfahren nach Ansprüchen 1 bis 5, dadurch gekennzeichnet, daß man 0,001 bis 5 Gew.-% Edelmetallkatalysator (gerechnet als Metall) einsetzt.

7. Verfahren nach Ansprüchen 1 bis 6, dadurch gekennzeichnet, daß man es kontinuierlich durchführt.

8. Verfahren nach Ansprüchen 1 bis 6, dadurch gekennzeichnet, daß man es diskontinuierlich durchführt.

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Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betrifft Anspruch	KLASSIFIKATION DER ANMELDUNG (Int.Cl.6)
X	EP-A-0 587 896 (DAIKIN INDUSTRIES LTD.) * Seite 1, Zeile 7 - Zeile 11 *	1	C07C17/354 C07C19/08
A	EP-A-0 442 087 (BAYER AG) * Ansprüche 1-8 *	1	
A	DATABASE WPI Week 9329 Derwent Publications Ltd., London, GB; AN 93-232277 & JP-A-05 155 788 (DAIKIN KOGYO KK) * Zusammenfassung *	1	

RECHERCHIERTE SACHGEBIETE (Int.Cl.6)

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KATEGORIE DER GENANNTEN DOKUMENTE

X : von besonderer Bedeutung allein betrachtet
Y : von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung derselben Kategorie
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(71) Déposant *(pour tous les États désignés sauf US)* : **ARKEMA FRANCE** [FR/FR]; 420, rue d'Estienne d'Orves, F-92700 Colombes (FR).

(72) Inventeurs; et

(75) Inventeurs/Déposants *(pour US seulement)* : **DEVIC, Michel** [FR/FR]; 22, rue Georges Clémenceau, F-69110 Sainte Foy Les Lyon (FR). **DOUCET, Nicolas** [FR/FR]; 373, rue Garibaldi, F-69007 Lyon (FR). **WENDLINGER, Laurent** [FR/FR]; 18, Hameau des Pierres Blanches, F-69510 Soucieu En Jarrest (FR). **CAVALLINI, Géraldine** [FR/FR]; 5, rue Henri Moissan, F-69360 Saint Symphorien D'ozon (FR). **SEDAT, Pierre-Marie** [FR/FR]; 65, rue des Glycines, F-69210 FLEURIEUX sur L'ARBRESLE (FR). **AVRIL, Karine** [FR/FR]; 8, rue Vauban, F-69006 Lyon (FR).

(74) Mandataire : **DANG, Doris**; Arkema France, Departement Propriete Industrielle, 420, rue d'Estienne d'Orves, F-92705 Colombes Cedex (FR).

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(54) **Title** : METHOD FOR PREPARING FLUORINE COMPOUNDS

(54) **Titre** : PROCEDE DE PREPARATION DE COMPOSES FLUORES

(57) **Abstract** : The invention relates to a method for preparing fluoropropenes of formula (I) $CF_3CF=CHR$, where R is a hydrogen or fluorine atom from at least one compound of formula (Ia) $CF_3CF=CFR$, where R has the same meaning as in formula (I), said method including the following steps: (i) hydrogenating at least one compound of formula (Ia) in an adiabatic reactor in the presence of a catalyst with a superstoichiometric amount of hydrogen so as to produce a hydrofluoropropane; (ii) partially condensing the flow from the adiabatic reactor of step (i) so as to produce a gaseous phase fraction, including unreacted hydrogen and a portion of the formed hydrofluoropropane, which is recirculated to step (i), and a liquid phase fraction including the residue of the hydrofluoropropane; (iii) dehydrofluorinating hydrofluoropropane from the liquid fraction of step (ii) using potassium hydroxide in an aqueous reaction medium contained in an agitated reactor so as to produce the fluoropropene of formula (I); and (iv) purifying the fluoropropene obtained in step (iii).

(57) **Abrégé** : L'invention a pour objet un procédé de préparation de fluoropropènes de formule (I) $CF_3CF=CHR$ dans laquelle R représente un atome d'hydrogène ou de fluor à partir d'au moins un composé de formule (Ia) $CF_3CF=CFR$ dans laquelle R a la même signification que dans la formule (I) comprenant les étapes suivantes: (i) hydrogénation d'au moins un composé de formule (Ia) dans un réacteur adiabatique en présence d'un catalyseur avec de l'hydrogène présent en quantité surstochiométrique pour donner un hydrofluoropropane; (ii) condensation partielle du flux issu du réacteur adiabatique de l'étape (i) pour donner une fraction en phase gazeuse, comprenant de l'hydrogène non réagi et une partie d' hydrofluoropropane formé, qui est recyclée à l'étape (i) et une fraction en phase liquide comprenant le reste de l' hydrofluoropropane; (iii) déhydrofluoration d' hydrofluoropropane provenant de la fraction liquide de l'étape (ii) à l'aide d'hydroxyde de potassium dans un milieu réactionnel aqueux contenu dans un réacteur agité pour donner le fluoropropène de formule (I); et (iv) purification du fluoropropène obtenu à l' étape (iii).

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PROCEDE DE PREPARATION DE COMPOSES FLUORES

L'invention a pour objet un procédé de préparation de composés oléfiniques fluorés.

Les hydrofluorocarbones (HFC) et en particulier les hydrofluorooléfines, telles que le 2,3,3,3-tétrafluoro-1-propène (HFO 1234yf) sont des composés connus pour leurs propriétés de réfrigérants et fluides caloporteurs, extinctrices, propulseurs, agents moussants, agents gonflants, diélectriques gazeux, milieu de polymérisation ou monomère, fluides supports, agents pour abrasifs, agents de séchage et fluides pour unité de production d'énergie. A la différence des CFC (chlorofluorocarbones) et des HCFC(hydrochlorofluorocarbones), qui sont potentiellement dangereux pour la couche d'ozone, les HFOs ne contiennent pas de chlore et donc ne posent pas de problème pour la couche d'ozone.

Le 1,2,3,3,3- pentafluoropropène (HFO-1225ye) est un intermédiaire de synthèse dans la fabrication du 2,3,3,3-tétrafluoro-1-propène (HFO-1234yf).

On connaît plusieurs procédés de fabrication de composés oléfiniques fluorés.

Le document Knunyants et al, Journal of the USSR Academy of Sciences, Chemistry Department, "reactions of fluoro-olefins", report 13., "catalytic hydrogenation of perfluoro-olefins", 1960, décrit de façon distincte diverses réactions chimiques sur des composes fluorés. Ce document décrit l'hydrogénation sensiblement quantitative de l'hexafluoropropène (HFP) sur un catalyseur à base de palladium supporté sur alumine, la température passant de 20°C à 50°C, puis étant maintenue à cette valeur. Ce document décrit la déhydrofluoration du 1,1,1,2,3,3-

hexafluoropropane (HFC-236ea) par passage au travers d'une suspension de KOH dans l'éther de dibutyle, pour produire du 1,2,3,3,3-pentafluoropropène-1 (HFO-1225ye) avec un rendement de 60 % seulement. Ce document décrit l'hydrogénation du 1,2,3,3,3-pentafluoropropène-1 (HFO-1225ye) en 1,1,1,2,3-pentafluoropropane (HFC-245eb) sur un catalyseur palladium supporté sur alumine. Au cours de cette hydrogénation il se produit aussi une réaction d'hydrogénolyse, une quantité significative de 1,1,1,2-tetrafluoropropane étant produite. Ce document décrit la déhydrofluoration de 1,1,1,2,3-pentafluoropropane (HFC-245eb) en 2,3,3,3-tétrafluoro-1-propène (HFO-1234yf) par passage dans une suspension de KOH en poudre dans l'éther de dibutyle avec un rendement de 70 % seulement. Ces réactions sont décrites indépendamment les unes des autres, mêmes s'il est indiqué qu'il est possible de les combiner pour synthétiser une gamme de dérivés d'éthylène, propylène et isobutylène contenant des quantités variables de fluor.

Le document US-P-5396000 décrit la préparation de 1,1,1,2,3-pentafluoropropane par déhydrofluoration catalytique de 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) en 1,2,3,3,3-pentafluoropropène-1 (HFO-1225ye), suivi d'une hydrogénation pour produire le composé recherché. La déshydrohalogénation du HFC-236ea en HFO-1225ye est effectuée en phase gazeuse, le produit de la réaction étant, dans un exemple, envoyé directement au réacteur suivant dans lequel a lieu l'hydrogénation du composé HFO-1225ye en composé HFC-245eb. Il est aussi indiqué dans ce document que le composé HFC-236ea peut être obtenu par hydrogénation de hexafluoropropylène (HFP).

Le document US-P-5679875 décrit la préparation de 1,1,1,2,3-pentafluoropropane par déhydrofluoration

catalytique de 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) en 1,2,3,3,3-pentafluoropropène-1 (HFO-1225ye), suivi d'une hydrogénation pour produire le composé recherché. Les réactions sont effectuées en phase gaz. Il est aussi indiqué dans ce document que le composé HFC-236ea peut être obtenu par hydrogénation de hexafluoropropylène (HFP).

Le document WO 2008/030440 décrit la préparation du HFO-1234yf à partir du HFO-1225ye en faisant réagir le HFO-1225ye avec de l'hydrogène en présence d'un catalyseur pour donner le HFC-245eb, puis en faisant réagir le HFC-245eb soit avec une solution aqueuse basique en présence d'un catalyseur de transfert de phase et un solvant non-aqueux, non-alcoolique soit en phase gazeuse en présence d'un catalyseur. La réaction d'hydrogénation peut être mise en œuvre à une température comprise entre 50 et 300°C ou entre 50 et 200°C.

Le document WO 2008/030440 suggère l'emploi d'un réacteur tubulaire pour l'étape d'hydrogénation du HFO-1225ye. Ce document est complètement silencieux sur l'exothermicité de la réaction d'hydrogénation ou la durée de vie du catalyseur.

Le document WO 2008/057794 décrit un procédé de fabrication de composés oléfiniques fluorés ayant de trois à six atomes de carbone et un degré de substitution d'halogène N comprenant (i) la conversion en au moins deux étapes réactionnelles d'une matière première oléfinique fluorée ayant le même nombre de carbone que le composé oléfinique fluoré recherché mais un degré de substitution d'halogène N+1 pour donner un alcane fluoré ayant un degré de substitution d'halogène N+1 et (ii) la conversion de l'alcane fluoré produite en (i) en composés oléfiniques fluorés recherchés.

Selon le document WO 2008/057794, l'utilisation de plusieurs étapes de la conversion (i) pour donner l'alcane fluoré a pour but d'augmenter la conversion et la sélectivité.

Le Tableau 1 de ce document illustre la conversion (i) en au moins quatre étapes avec des températures différentes et de quantités de catalyseur différentes pour chaque étapes.

La conversion (i) en plusieurs étapes du document WO 2008/057794 n'est pas facile à mettre en œuvre à l'échelle industrielle.

Il existe un besoin d'un procédé de préparation de composés oléfiniques fluorés intégré dont la mise en œuvre à l'échelle industrielle est plus aisée et/ou fiable tout en permettant d'obtenir des composés oléfiniques fluorés de haute pureté avec de bon rendement .

L'invention fournit donc un procédé de préparation de fluoropropènes de formule (I) : $CF_3CF=CHR$ dans laquelle R représente un atome d'hydrogène ou de fluor à partir d'au moins un composé de formule (Ia) $CF_3CF=CFR$ dans laquelle R a la même signification que dans la formule (I), comprenant les étapes suivantes :

(i)hydrogénation dans un réacteur adiabatique en présence d'un catalyseur d'au moins un composé de formule (Ia) avec de l'hydrogène en quantité surstoechiométrique pour donner au moins un hydrofluoropropane;

(ii)condensation partielle du flux issu du réacteur adiabatique de l'étape (i) pour donner une fraction en phase gaz, comprenant de l'hydrogène non réagi et une partie d' hydrofluoropropane formé à l'étape (i), qui est recyclée à l'étape d'hydrogénation et une fraction en phase

liquide comprenant le reste d'hydrofluoropropane formé en (i);

(iii)déhydrofluoration de l'hydrofluoropropane provenant de la fraction liquide de l'étape (ii) à l'aide d'hydroxyde de potassium (KOH) dans un milieu réactionnel aqueux contenu dans un réacteur agité pour donner le fluoropropène de formule (I); et

(iv) purification du fluoropropène de formule (I).

Le procédé selon la présente invention peut comprendre en outre:

- une étape de traitement du sel de potassium co-produit à l'étape de déhydrofluoration (iii)pour régénérer l'hydroxyde de potassium
- une étape de chauffage du flux gazeux recyclé au réacteur adiabatique.

Selon un mode de réalisation de la présente invention, le 1,2,3,3,3-pentafluoropropène est obtenu à partir de l'hexafluoropropène.

Selon un autre mode de réalisation de la présente invention, le 2,3,3,3-tétrafluoro-1-propène est obtenu à partir du 1,2,3,3,3-pentafluoropropène.

Le procédé selon la présente invention peut être mis en œuvre en discontinu, semi-continu ou continu. Avantageusement, le procédé est mis en œuvre en continu.

La demanderesse a constaté que le recyclage d'une partie d'hydrofluoropropane formé en (i) permet de contrôler la forte exothermicité de la réaction d'hydrogénation de l'étape (i) et ainsi améliorer la durée de vie du catalyseur. En outre, la condensation partielle de l'étape (ii) permet d'éviter l'entraînement de l'hydrogène dans les étapes ultérieures facilitant ainsi la

récupération du fluoropropène de haute pureté avec un bon rendement.

Etape d'hydrogénation (i)

L'étape d'hydrogénation peut être mise en œuvre en présence d'un rapport molaire H_2/composé de formule (Ia) compris entre 1,1 et 40, de préférence compris entre 2 et 15.

L'étape d'hydrogénation peut être mise en œuvre à pression comprise entre 0,5 et 20 bars absolu et de préférence entre 1 et 5 bars absolu.

Comme catalyseurs susceptibles d'être utilisés dans l'étape d'hydrogénation, on peut notamment citer les catalyseurs à base d'un métal du groupe VIII ou rhénium, éventuellement supporté, par exemple sur carbone, carbure de silicium, alumine, fluorure d'aluminium.

Comme métal, on peut utiliser du platine ou du palladium, en particulier du palladium, avantageusement supporté sur carbone ou alumine. On peut aussi associer ce métal avec un autre métal comme l'argent, le cuivre, l'or, le tellure, le zinc, le chrome, le molybdène et le thallium.

Le catalyseur peut être présent sous toute forme appropriée, extrudés, pastilles ou billes.

De préférence, on utilise un catalyseur comprenant entre 0,05 et 10% en poids et avantageusement entre 0,1 et 5% en poids de palladium supporté sur de l'alumine ou carbone.

L'étape d'hydrogénation peut être mise en œuvre dans des conditions telles que la température à l'entrée du réacteur adiabatique est comprise entre 30 et 200 °C, de préférence entre 40 et 140°C et celle à la sortie du

réacteur adiabatique est comprise entre 50 et 250°C, de préférence entre 80 et 160°C.

Le temps de contact (rapport entre le volume de catalyseur et le flux total gazeux dans les conditions normales de température et de pression) est de préférence compris entre 0,2 et 10 secondes et avantageusement entre 1 et 5 secondes.

Cette étape d'hydrogénation peut être mise en œuvre dans un réacteur adiabatique multiétagé.

L'étape d'hydrogénation du composé de formule (Ia) est sensiblement quantitative.

Etape de condensation (ii)

Le flux à l'issue de l'étape d'hydrogénation (i) est soumis à une étape de condensation dans des conditions telles que l'hydrogène non réagi n'est pas condensé et qu'une partie d'hydrofluoroalcane formé à l'étape (i) est condensé.

De préférence, l'étape de condensation est mise en œuvre à une température comprise entre 0 et 50°C et à une pression comprise entre 0,5 et 20 bar absolu, avantageusement entre 1 et 5 bars absolu.

De préférence, l'étape de condensation est mise en œuvre dans des conditions telles qu' entre 1 et 30 % de l'hydrofluoroalcane en sortie du réacteur à l'étape (i) est condensé et avantageusement entre 2 et 10 % est condensé.

La fraction non condensée est ensuite recyclée à l'étape d'hydrogénation (i) après un éventuel chauffage.

Etape de déhydrofluoration (iii)

La fraction condensée comprenant de l'hydrofluoropropane, après vaporisation, est ensuite soumise à une étape de déhydrofluoration à l'aide de

l'hydroxyde de potassium présent en quantité, de préférence comprise entre 20 et 75 % en poids et avantageusement comprise entre 55 et 70 % en poids par rapport au poids du mélange eau et KOH du milieu réactionnel aqueux contenu dans le réacteur agité.

Le milieu réactionnel aqueux de l'étape de déhydrofluoration est de préférence maintenu à une température comprise entre 80 et 180 °C, avantageusement comprise entre 125 et 180°C. Une température du milieu réactionnel particulièrement préférée est comprise entre 145 et 165°C.

L' étape de déhydrofluoration peut être mise en œuvre à une pression de 0,5 à 20 bars mais on préfère travailler à une pression comprise entre 0,5 et 5 bars absolus et plus avantageusement entre 1,1 et 2,5 bars absolus.

Lorsque le composé à hydrogéner est l'hexafluoropropène, l'étape de déhydrofluoration consiste à faire réagir le 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) avec de l'hydroxyde de potassium pour donner le 1,2,3,3,3-pentafluoropropène.

Lorsque le composé à hydrogéner est le 1,2,3,3,3-pentafluoropropène, l'étape de déhydrofluoration consiste à faire réagir le 1,1,1,2,3,-pentafluoropropane (HFC-245eb) avec de l'hydroxyde de potassium pour donner le 2,3,3,3-tetrafluoropropène.

Etape de traitement pour régénérer l'hydroxyde de potassium

Au cours de l'étape de déhydrofluoration, il se forme du fluorure de potassium.

Le procédé selon la présente invention peut comprendre une étape de traitement au cours de laquelle le fluorure de potassium co-produit à l'étape de déhydrofluoration est mis

en contact avec de l'hydroxyde de calcium dans un milieu réactionnel aqueux à une température de préférence comprise entre 50 et 150 °C et avantageusement comprise entre 70 et 120°C et plus avantageusement entre 70 et 100°C.

Cette étape de traitement est de préférence mise en œuvre en introduisant de l'hydroxyde de calcium dans un réacteur contenant une partie du milieu réactionnel, provenant de l'étape de déhydrofluoration et comprenant du fluorure de potassium, de l'hydroxyde de potassium et de l'eau après éventuelle dilution.

Le fluorure de potassium est de préférence présent entre 4 et 45 % en poids par rapport au milieu réactionnel provenant de l'étape de déhydrofluoration (iii).

Le milieu réactionnel du traitement comprend de préférence entre 4 et 50 % en poids d'hydroxyde de potassium et avantageusement entre 10 et 35 % en poids d'hydroxyde de potassium par rapport au poids total d'hydroxyde de potassium et eau dans le milieu.

L'étape de traitement avec l'hydroxyde de calcium permet de régénérer de l'hydroxyde de potassium qui peut être recyclé à l'étape de déhydrofluoration et d'obtenir du fluorure de calcium de qualité commerciale valorisable après séparation par exemple filtration et décantation.

Du fluorure de calcium de taille moyenne comprise entre 20 et 35 µm (taille moyenne à 50 % en poids de la distribution granulométrique)est obtenu dans les conditions préférées de cette étape de traitement.

L'étape de traitement à l'hydroxyde de calcium peut être mise en œuvre dans tout type de réacteur connu de l'homme de l'art, par exemple un réacteur agité.

Etape de purification du fluoropropène de formule (I)

Le flux gazeux à l'issue de l'étape de déhydrofluoration (iii) comprenant le fluoropropène de formule (I), le composé de formule (Ia) non réagi et les sous produits est soumis à une étape de purification pour obtenir des fluoropropènes de haute pureté.

La purification comprend de préférence une première étape de distillation pour séparer les impuretés légères et une deuxième étape de distillation pour séparer le fluoropropène de formule (I) des impuretés lourdes.

En l'absence de l'étape de condensation (ii), de l'hydrogène se retrouve dans les impuretés légères de la première étape de distillation.

Lorsque le produit recherché est le 1,2,3,3,3-pentafluoropropène, les impuretés légères à éliminer comprend le trifluorure de vinyle.

Lorsque le produit recherché est le 2,3,3,3-tetrafluoropropène, les impuretés légères à éliminer comprend le trifluoropropyne.

Lorsque le produit recherché est le 1,2,3,3,3-pentafluoropropène, les impuretés lourdes à éliminer comprennent le 1,1,1,2,3,3 hexafluoropropane (HFC-236ea) qui peut être recyclé à l'étape (iii).

Lorsque le produit recherché est le 2,3,3,3-tetrafluoropropène, les impuretés lourdes à éliminer comprennent le 1,1,1,2,3 pentafluoropropane (HFC-245eb) qui peut être recyclé à l'étape (iii).

On rappellera que:

- le taux de conversion est le % du produit de départ ayant réagi (nombre mole de produit départ ayant réagi/nombre mole produit départ introduit) ;

- la sélectivité en produit recherché est le ratio nombre de mole de produit recherché formé/nombre mole produit départ ayant réagi ;

EXEMPLE

L'exemple suivant illustre l'invention sans la limiter.

Synthèse du HFO-1225ye par hydrogénation de l'HFP en HFC-236ea puis déhydrofluoration du HFC-236ea en HFO-1225ye.

Hydrogénation de HFP en HFC-236ea

On utilise un réacteur tubulaire en inox de diamètre interne 2,1 cm et longueur 120 cm contenant 479 g, soit 330 cm^3 de catalyseur sous forme d'un lit fixe. Le catalyseur contient 0,2 % en poids de palladium supporté sur alumine α.

Pendant la durée de la réaction, on injecte en continu environ 0,71 mol/h d'hydrogène et 0,7 mol/h de hexafluoropropène. La pression est de 2 bar absolue. Le ratio molaire hydrogène/HFP à l'entrée du réacteur est de 6. La température à l'entrée de réacteur est de 43,2 ° C et la température maximale atteinte au cours de la réaction est de 122,3 ° C. Le temps de contact suivant la définition donnée ci-dessus est de 2,8 s.

On obtient une conversion de 100% en HFP avec une sélectivité en HFC-236ea supérieure à 99%.

Le flux en sortie de réacteur est refroidi à 17,6°C et partiellement condensé. La phase gaz est recyclée au réacteur après avoir été préalablement préchauffée. La phase liquide, représentant 5% du HFC-236ea présent en sortie du réacteur, est composée à plus de 99% de HFC-236ea. Elle est vaporisée avant d'alimenter le réacteur de dehydrofluoration.

Déshydrofluoration du HFC-236ea en HFO-1225ye

On utilise un réacteur agité de 3 litres en inox de diamètre interne 1,5 cm et contenant 2,6 litres d'une solution de potasse à 60 % environ en poids.

Pendant la durée de la réaction, on injecte en continu environ 0,7 mol/h de HFC-236ea gaz et 6,4 mol/h environ d'une solution liquide de potasse à 70 % environ en poids de KOH (soit 2,7 mol/h de KOH pur). La pression est de 1,1 bar absolue.

La température à l'entrée de réacteur est de 160 °C.

On obtient une conversion de 98% en HFC-236ea avec une sélectivité en HFO-1225ye(E+Z) supérieure à 99%. La pureté du HFO-1225ye (E+Z) est supérieure à 97%.

REVENDICATIONS

1. Procédé de préparation de fluoropropènes de formule (I) : $CF_3CF=CHR$ dans laquelle R représente un atome d'hydrogène ou de fluor à partir d'au moins un composé de formule (Ia) $CF_3CF=CFR$ dans laquelle R a la même signification que dans la formule (I), comprenant les étapes suivantes :

(i) hydrogénation dans un réacteur adiabatique en présence d'un catalyseur d'au moins un composé de formule (Ia) avec de l'hydrogène en quantité surstoechiométrique pour donner au moins un hydrofluoropropane;

(ii) condensation partielle du flux issu du réacteur adiabatique de l'étape (i) pour donner une fraction en phase gaz, comprenant de l'hydrogène non réagi et une partie d' hydrofluoropropane formé à l'étape (i), qui est recyclée à l'étape d'hydrogénation et une fraction en phase liquide comprenant le reste d'hydrofluoropropane formé en (i);

(iii) déhydrofluoration de l'hydrofluoropropane provenant de la fraction liquide de l'étape (ii) à l'aide d'hydroxyde de potassium (KOH) dans un milieu réactionnel aqueux contenu dans un réacteur agité pour donner le fluoropropène de formule (I); et

(iv) purification du fluoropropène de formule (I).

2. Procédé selon la revendication 1, dans lequel le rapport molaire hydrogène / composé de formule (Ia) est compris entre 1,1 et 40, de préférence compris entre 2 et 15.

3. Procédé selon la revendication 1 ou 2, dans lequel la température à l'entrée du réacteur adiabatique de l'étape (i) est comprise entre 30 et 200°C, de préférence entre 40 et 140 °C et celle à la sortie comprise entre 50 et 250°C, de préférence entre 80 et 160°C.

4. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que la pression est comprise entre 0,5 et 20 bars absolu, de préférence entre 1 et 5 bars absolu.

5. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que l'étape de condensation (ii) est mise en œuvre à une température comprise entre 0 et 50 °C et une pression comprise entre 0,5 et 20 bar absolu, de préférence entre 1 et 5 bar absolu.

6. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que l'hydroxyde de potassium représente entre 20 et 75 %, de préférence entre 55 et 70% en poids du mélange eau-hydroxyde de potassium de l'étape (iii).

7. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que le milieu réactionnel de l'étape de déhydrofluoration (iii) est mis en œuvre à une température comprise entre 125 et 180°C, de préférence comprise entre 145 et 165°C.

8. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce qu'il comprend une étape de traitement au cours de laquelle le fluorure de potassium,

co-produit dans l'étape de déhydrofluoration réagit avec de l'hydroxyde de calcium, pour régénérer de l'hydroxyde de potassium.

9. Procédé selon la revendication 8 caractérisé en ce que l'hydroxyde de potassium représente entre 4 et 50 % en poids par rapport au poids total d'hydroxyde de potassium et eau du milieu réactionnel aqueux de l'étape de traitement.

10. Procédé selon la revendication 8 ou 9 caractérisé en ce la température de traitement est comprise entre 50 et 150°C, de préférence entre 70 et 120°C.

11. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que la purification de l'étape (iv) comprend une première distillation pour éliminer les impuretés légères et une deuxième distillation pour éliminer les impuretés lourdes.

12. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce qu'il comprend l'hydrogénation de l'hexafluoropropène pour donner du 1,1,1,2,3,3-hexafluoropropane qui est ensuite déhydrofluoré pour donner le 1,2,3,3,3-pentafluoropropène.

13. Procédé selon l'une quelconque des revendications 1 à 11 caractérisé en ce qu'il comprend l'hydrogénation du 1,2,3,3,3-pentafluoropropène pour donner du 1,2,3,3,3-pentafluoropropane qui est ensuite déhydrofluoré pour donner le 2,3,3,3-tetrafluoropropène.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FR2010/050990

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C17/25 C07C21/18
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 practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KNUNYANTS I L ET AL: "Reactions of fluoro olefins. XIII. Catalytic hydrogenation of perfluoro olefins" IZVESTIA AKADEMII NAUK SSSR. SERIA HIMICESKAA, MOSCOW, RU, 1 January 1960 (1960-01-01), pages 1312-1318, XP002548816 ISSN: 0002-3353 cited in the application Schéma au milieu de la page 1313 *exemples* ----- -/--	1-13

[X] Further documents are listed in the continuation of Box C.

[X] 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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 September 2010	24/09/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Panday, Narendra

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2008/030440 A2 (DU PONT [US]; RAO VELLIYUR NOTT MALLIKARJUNA [US]; SIEVERT ALLEN CAPRO) 13 March 2008 (2008-03-13) cited in the application * abstract examples 1-7 claim 1 page 13, line 30 - page 14, line 1	1-13
Y	WO 2008/030439 A2 (DU PONT [US]; RAO VELLIYUR NOTT MALLIKARJUNA [US]; SIEVERT ALLEN CAPRO) 13 March 2008 (2008-03-13) claims 1,4 examples 1-3	1-13
Y	US 2005/090698 A1 (MERKEL DANIEL C [US] ET AL MERKEL DANIEL C [US] ET AL) 28 April 2005 (2005-04-28) * abstract claims 1,3,5 examples 1,2	1-13
Y	SIANESI DARIO ET AL: "Fluoro olefins. I. cis- and trans-1,2,3,3,3-Pentafluoropropylene" ANNALI DI CHIMICA, SOCIETA CHIMICA ITALIANA, ROME, IT, vol. 55, no. 8-9, 1 January 1965 (1965-01-01), pages 850-861, XP009092725 ISSN: 0003-4592 page 853 - paragraph b)	1-13
Y	WO 2009/084703 A1 (DAIKIN IND LTD [JP]; TAKAHASHI KAZUHIRO [JP]; SHIBANUMA TAKASHI [JP]) 9 July 2009 (2009-07-09) * abstract claim 1 figure 1 page 16, line 7 - line 9	1-13
Y	WO 2009/003157 A1 (ARKEMA INC [US]; ELSHEIKH MAHER Y [US]; BONNET PHILIPPE [US]; WENDLING) 31 December 2008 (2008-12-31) example 7; table 2	1-13
Y	WO 2008/075017 A2 (INEOS FLUOR HOLDINGS LTD [GB]; SHARRATT ANDREW PAUL [GB]; LOW ROBERT E) 26 June 2008 (2008-06-26) examples 1-22 figures 1,2 claims 1,5,10	1-13

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2009/138764 A1 (INEOS FLUOR HOLDINGS LTD [GB]; SMITH JOHN WILLIAM [GB]; MCGUINESS CLAI) 19 November 2009 (2009-11-19) * abstract claims 1,17-21 figures 1-3 the whole document	1-13
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X,P	WO 2010/029240 A1 (ARKEMA FRANCE [FR]; PIGAMO ANNE [FR]; DEVIC MICHEL [FR]; WENDLINGER LA) 18 March 2010 (2010-03-18) * abstract claim 1 examples 1-6	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FR2010/050990

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WO 2008030440 A2	13-03-2008	CN 101535227 A	16-09-2009
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RAPPORT DE RECHERCHE INTERNATIONALE

Demande internationale n°
PCT/FR2010/050990

A. CLASSEMENT DE L'OBJET DE LA DEMANDE
INV. C07C17/25 C07C21/18
ADD.

Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB

B. DOMAINES SUR LESQUELS LA RECHERCHE A PORTE

Documentation minimale consultée (système de classification suivi des symboles de classement)
C07C

Documentation consultée autre que la documentation minimale dans la mesure où ces documents relèvent des domaines sur lesquels a porté la recherche

Base de données électronique consultée au cours de la recherche internationale (nom de la base de données, et si cela est réalisable, termes de recherche utilisés)
EPO-Internal

C. DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie*	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
Y	KNUNYANTS I L ET AL: "Reactions of fluoro olefins. XIII. Catalytic hydrogenation of perfluoro olefins" IZVESTIA AKADEMII NAUK SSSR. SERIA HIMICESKAA, MOSCOW, RU, 1 janvier 1960 (1960-01-01), pages 1312-1318, XP002548816 ISSN: 0002-3353 cité dans la demande Schéma au milieu de la page 1313 *exemples* ----- -/--	1-13

[X] Voir la suite du cadre C pour la fin de la liste des documents

[X] Les documents de familles de brevets sont indiqués en annexe

* Catégories spéciales de documents cités:

"A" document définissant l'état général de la technique, non considéré comme particulièrement pertinent

"E" document antérieur, mais publié à la date de dépôt international ou après cette date

"L" document pouvant jeter un doute sur une revendication de priorité ou cité pour déterminer la date de publication d'une autre citation ou pour une raison spéciale (telle qu'indiquée)

"O" document se référant à une divulgation orale, à un usage, à une exposition ou tous autres moyens

"P" document publié avant la date de dépôt international, mais postérieurement à la date de priorité revendiquée

"T" document ultérieur publié après la date de dépôt international ou la date de priorité et n'appartenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention

"X" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive par rapport au document considéré isolément

"Y" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est associé à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier

"&" document qui fait partie de la même famille de brevets

Date à laquelle la recherche internationale a été effectivement achevée	Date d'expédition du présent rapport de recherche internationale
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Nom et adresse postale de l'administration chargée de la recherche internationale	Fonctionnaire autorisé
Office Européen des Brevets, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040. Fax: (+31-70) 340-3016	Panday, Narendra

Formulaire PCT/ISA/210 (deuxième feuille) (avril 2005)

C(suite). DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie*	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
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Y	SIANESI DARIO ET AL: "Fluoro olefins. I. cis- and trans-1,2,3,3,3-Pentafluoropropylene" ANNALI DI CHIMICA, SOCIETA CHIMICA ITALIANA, ROME, IT, vol. 55, no. 8-9, 1 janvier 1965 (1965-01-01), pages 850-861, XP009092725 ISSN: 0003-4592 page 853 - alinéa b)	1-13
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Y	WO 2008/075017 A2 (INEOS FLUOR HOLDINGS LTD [GB]; SHARRATT ANDREW PAUL [GB]; LOW ROBERT E) 26 juin 2008 (2008-06-26) exemples 1-22 figures 1,2 revendications 1,5,10	1-13

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C(suite). DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie*	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
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RAPPORT DE RECHERCHE INTERNATIONALE

Renseignements relatifs aux membres de familles de brevets

Demande internationale n°
PCT/FR2010/050990

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WO 2010029240 A1	18-03-2010	CN 101671229 A	17-03-2010
		FR 2935703 A1	12-03-2010

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)

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0953701 4 juin 2009 (04.06.2009) FR

(71) Déposant *(pour tous les États désignés sauf US)* : **ARKEMA FRANCE** [FR/FR]; 420, rue d'Estienne d'Orves, F-92700 Colombes (FR).

(72) Inventeurs; et

(75) Inventeurs/Déposants *(pour US seulement)* : **GUILLET, Dominique** [FR/FR]; 262, rue de Corcelle, F-69390 Vernaison (FR). **DEVIC, Michel** [FR/FR]; 22, rue Georges Clémenceau, F-69110 Sainte Foy Les Lyon (FR).

(74) Mandataire : **DANG, Doris**; Arkema France, Departement Propriete Industrielle, 420, rue d'Estienne d'Orves, F-92705 Colombes Cedex (FR).

(81) États désignés *(sauf indication contraire, pour tout titre de protection nationale disponible)* : AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) États désignés *(sauf indication contraire, pour tout titre de protection régionale disponible)* : ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), eurasien (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), européen (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Déclarations en vertu de la règle 4.17 :

— *relative au droit du déposant de demander et d'obtenir un brevet (règle 4.17.ii))*

Publiée :

— *avec rapport de recherche internationale (Art. 21(3))*

— *avant l'expiration du délai prévu pour la modification des revendications, sera republiée si des modifications sont reçues (règle 48.2.h))*

WO 2010/139873 A1

(54) **Title** : PROCESS FOR PREPARING FLUOROOLEFIN COMPOUNDS

(54) **Titre** : PROCEDE DE PREPARATION DE COMPOSES FLUORES OLEFINIQUES

(57) **Abstract** : The subject matter of the invention is a process for preparing fluoroolefin compounds. The invention relates more particularly to a process for producing a (hydro)fluoroolefin compound, which comprises (i) bringing at least one compound comprising from three to six carbon atoms, at least two fluorine atoms and at least one hydrogen atom, on the condition that at least one hydrogen atom and one fluorine atom are located on adjacent carbon atoms, into contact with a solid reactant comprising calcium hydroxide.

(57) **Abrégé** : L'invention a pour objet un procédé de préparation de composés fluorés oléfiniques. Elle concerne plus particulièrement un procédé de fabrication d'un composé (hydro)fluorooléfinique comprenant (i) la mise en contact d'au moins un composé comprenant de trois à six atomes de carbone, d'au moins deux atomes de fluor et d'au moins un atome d'hydrogène, à la condition qu' au moins un atome d'hydrogène et un atome de fluor sont situés sur des atomes de carbone adjacent, avec un réactif solide comprenant de l'hydroxyde de calcium.

PROCEDE DE PREPARATION DE COMPOSES FLUORES OLEFINIQUES

DOMAINE DE L'INVENTION

L'invention a pour objet un procédé de préparation de composés fluorés oléfiniques. Elle concerne plus particulièrement un procédé de préparation des hydrofluoropropènes.

ARRIERE-PLAN TECHNOLOGIQUE

Les hydrofluorocarbones (HFC) et en particulier les hydrofluorooléfines (HFOs), telles que le 2,3,3,3-tétrafluoro-1-propène (HFO-1234yf) sont des composés connus pour leurs propriétés de réfrigérants et fluides caloporteurs, extinctrices, propulseurs, agents moussants, agents gonflants, diélectriques gazeux, milieu de polymérisation ou monomère, fluides supports, agents pour abrasifs, agents de séchage et fluides pour unité de production d'énergie. A la différence des CFC et des HCFC, qui sont potentiellement dangereux pour la couche d'ozone, les HFOs ne contiennent pas de chlore et donc ne posent pas de problème pour la couche d'ozone.

Le 1,2,3,3,3- pentafluoropropène (HFO-1225ye) est un intermédiaire de synthèse dans la fabrication du 2,3,3,3-tétrafluoro-1-propène (HFO-1234yf).

La plupart des procédés de fabrication des hydrofluorooléfines font appel à une réaction de déhydrohalogénation. Ainsi, le document WO 03/027051 décrit un procédé de fabrication de fluorooléfines de formule $CF_3CY=CX_nH_p$, dans laquelle X et Y représentent chacun un atome d'hydrogène ou d'halogène choisi parmi le fluor, le chlore, le brome ou l'iode ; n et p sont des nombres entiers et peuvent indépendamment prendre la valeur zéro, 1 ou 2 à condition que (n + p) = 2, comprenant la mise en contact d'un composé de formule $CF_3C(R^1_aR^2_b)C(R^3_cR^4_d)$ avec R^1, R^2, R^3 et R^4 représentant indépendamment un atome d'hydrogène ou d'halogène choisi parmi le fluor, le chlore, le brome ou l'iode à condition qu'au moins un de R^1, R^2, R^3 et R^4 est un atome d'halogène et qu'au moins un atome d'hydrogène et un atome d'halogène sont situés sur des atomes de carbone adjacent ; a et b peuvent indépendamment prendre la valeur zéro, 1 ou 2 à condition que (a + b) = 2 ; c et d peuvent indépendamment prendre la valeur zéro, 1, 2 ou 3 à condition que (c + d) = 3, avec au moins un hydroxyde de métal alcalin en présence d'un catalyseur de transfert phase.

Ce document enseigne à l'exemple 2, qu'en l'absence d'un catalyseur de transfert de phase, il n'y a pas de réaction lorsque le 1,1,1,3,3-pentafluoropropane

(HFC-245fa) est mis en contact avec une solution aqueuse de 50 % en poids de hydroxyde de potassium (KOH) pendant 24 heures à température ambiante et sous pression.

Ce document suggère en outre une température de réaction compris entre –20°C et 80°C mais ne recommande pas l'emploi des hydroxydes d'alcalino-terreux du fait de leur solubilité limitée dans l'eau.

Le document WO 2008/075017 divulgue un procédé de déhydrohalogénation comprenant la mise en contact d'un hydro(halo)fluoroalcane avec une base éventuellement en présence d'un solvant. Il enseigne qu'en l'absence d'un solvant, l'hydro(halo)fluoroalcane peut être envoyé sur la base à chaud ou à l'état fondu.

Ce document illustre la réaction de déhydrofluoration du 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) en 1,2,3,3,3-pentafluoropropène (HFO-1225ye) à 150°C en présence d'une solution aqueuse de 50 % en poids de KOH. En l'absence d'un catalyseur de transfert de phase, la conversion au bout de 3 heures et demie est de 57,8 % et la sélectivité en HFO-1225ye est de 52,4 % (essai 1). En présence d'un catalyseur de transfert de phase, cette conversion est atteinte au bout de 2,5 heures seulement et la sélectivité est pratiquement inchangée (essai 4). Comme indiqué au tableau 2 de ce document pour accroître la sélectivité en HFO-1225ye, il est nécessaire d'utiliser un solvant organique.

WO 2007/056194 décrit la préparation de HFO-1234yf par déhydrofluoration du 1,1,1,2,3-pentafluoropropane (HFC-245cb) soit avec une solution aqueuse de KOH soit en phase gazeuse en présence d'un catalyseur, notamment sur catalyseur à base de nickel, de carbone ou une combinaison de ceux-ci.

Dans le document WO 2008/030440 est décrit un mode de réalisation de déhydrofluoration du 1,1,1,2,3-pentafluoropropane à l'aide d'une solution aqueuse basique en présence d'un solvant non aqueux, non alcoolique dans lequel le HFC-245eb est partiellement miscible.

Le document Knunyants et al, Journal of the USSR Academy of Sciences, Chemistry Department, "reactions of fluoro-olefins", report 13., "catalytic hydrogenation of perfluoro-olefins", 1960, décrit de façon distincte diverses réactions chimiques sur des composés fluorés. Ce document décrit la déhydrofluoration du 1,1,1,2,3,3-hexafluoropropane (236ea) par passage au travers d'une suspension de KOH

en poudre dans l'éther de dibutyle, pour produire du 1,2,3,3,3-pentafluoropropène-1 (HFO-1225ye) avec un rendement de 60 % seulement. Ce document décrit également la déhydrofluoration de 1,1,1,2,3-pentafluoropropane (HFC-245eb) en 2,3,3,3-tétrafluoro-1-propène (HFO-1234yf) par passage dans une suspension de KOH en poudre dans l'éther de dibutyle avec un rendement de 70 % seulement.

Enfin, l'article de Sianesi Dario et al. dans Annali Di Chimica, Societa Chimica Italiana, Rome, IT, vol. 55 no.8-9, 1 janvier 1965 pages 850-861 décrit la déhydrofluoration du 1,1,1,2,3,3-hexafluoropropane à l'aide du KOH.

Les réactions de déhydrofluoration telles que décrites ci-dessus conduisent, outre au composé hydrofluorooléfinique recherché, à la formation de l'eau et de fluorure de potassium. Par ailleurs, la mise en œuvre d'une telle réaction en continu n'est pas aisée à l'échelle industrielle car au moins trois phases (gazeuse, liquide et solide) sont mis en jeu et l'élimination du fluorure de potassium formé en quantité stœchiométrique pose problème .

La présente invention fournit un procédé de fabrication continu ou semi-continu d'un composé (hydro)fluorooléfinique permettant de remédier aux inconvénients précités. La réaction mise en jeu dans le procédé est une réaction gaz-solide.

La présente invention a donc pour objet un procédé de fabrication continu ou semi-continu d'un composé (hydro)fluorooléfinique comprenant (i) la mise en contact d'au moins un composé comprenant de deux à six atomes de carbone, d'au moins deux atomes de fluor et d'au moins un atome d'hydrogène, à la condition qu'au moins un atome d'hydrogène et un atome de fluor soient situés sur des atomes de carbone adjacent, avec un réactif solide comprenant de l'hydroxyde de calcium avec co-formation du fluorure de calcium, sous produit valorisable.

Le procédé selon la présente invention fournit de préférence un composé (hydro)fluorooléfinique comportant trois atomes de carbone, avantageusement un composé (hydro)fluorooléfinique représenté par la formule (I)

$$CF_3CY=CX_nH_p \qquad (I)$$

dans laquelle Y représente un atome d'hydrogène ou d'halogène choisi parmi le fluor, le chlore, le brome ou l'iode et X représente un atome d'halogène choisi parmi le fluor, le chlore, le brome ou l'iode ; n et p sont des nombres entiers et peuvent indépendamment prendre la valeur zéro, 1 ou 2 à condition que (n + p) = 2, en mettant en contact un

composé de formule $CF_3CYRCR'X_nH_p$, dans laquelle X, Y, n et p ont la même signification que dans la formule (I) et R représente un atome de fluor lorsque R' représente un atome d'hydrogène ou R représente un atome d'hydrogène lorsque R' représente un atome de fluor, avec un réactif solide comprenant de l'hydroxyde de calcium.

La présente invention convient tout particulièrement à la fabrication d'un composé de formule (Ia)

CF_3-CF=CHZ (Ia)

dans laquelle Z représente un atome d'hydrogène ou fluor à partir d'un composé de formule $CF_3CFRCHR'Z$ dans laquelle Z a la même signification que dans la formule (Ia) et R représente un atome de fluor lorsque R' représente un atome d'hydrogène ou R représente un atome d'hydrogène lorsque R' représente un atome de fluor.

Ainsi, le 2,3,3,3-tetrafluoropropène peut être obtenu par déhydrofluoration du 1,2,3,3,3-pentafluoropropane avec un réactif solide comprenant de l'hydroxyde de calcium et/ou le 1,2,3,3,3-pentafluoropropène par déhydrofluoration du 1,1,1,2,3,3-hexafluoropropane avec un réactif solide comprenant de l'hydroxyde de calcium. Le 1,2,3,3,3-pentafluoropropène peut être sous la forme d'isomère cis et/ou trans.

La présente invention peut en outre être utilisée pour la fabrication du 1,3,3,3-tetrafluoropropène par déhydrofluoration du 1,1,3,3,3-pentafluoropropane avec un réactif solide comprenant de l'hydroxyde de calcium.

Dans le procédé selon la présente invention le réactif solide peut contenir essentiellement de l'hydroxyde de calcium ou peut comprendre de l'hydroxyde de calcium en majorité et d'autres hydroxydes métalliques comme NaOH, KOH, $Mg(OH)_2$ et $Ba(OH)_2$.

On peut avantageusement utiliser comme réactif solide la chaux sodée (Soda lime) qui est de l'hydroxyde de calcium contenant quelques pour cent en poids de NaOH et de KOH.

La teneur en KOH dans le réactif solide est de préférence comprise entre 0,1 et 5 % en poids et avantageusement comprise entre 2 et 4 % en poids.

La teneur en NaOH dans le réactif solide est de préférence comprise entre 0,1 et 5 % en poids et avantageusement comprise entre 1 et 3 % en poids.

Le réactif solide, comprenant de l'hydroxyde de calcium, peut être utilisé sous forme de poudre ou de préférence sous forme de granulés et présentant avantageusement une porosité élevée. Une granulométrie de granulés comprise entre 1 et 10 mm est préférée.

Le taux d'humidité présent dans le réactif solide est de préférence compris entre 1 et 20 % en poids et avantageusement compris entre 7 à 20 % en poids et plus particulièrement compris entre 10 et 15 % en poids.

A titre d'exemple de réactif solide, on peut citer la chaux sodée, notamment celle commercialisée par la société GRACE sous la marque SODASORB HP.

Le procédé selon la présente invention est de préférence mis en œuvre à une température comprise entre 100 et 170° C, avantageusement comprise entre 120 et 150 ° C. Une température comprise entre 130 et 140° C est particulièrement préférée. La réaction de déhydrofluoration, selon le procédé de la présente invention, peut être mise en œuvre à pression atmosphérique mais on préfère travailler à une pression supérieure à la pression atmosphérique, par exemple entre 1 et 10 bars absolu. Avantageusement, cette pression est comprise entre 5 et 10 bars absolu.

La réaction peut être mise en œuvre selon les moyens habituels utilisés dans l'industrie pour effectuer une réaction entre un gaz et un solide, comme par exemple dans un réacteur en lit fluidisé avec le réactif solide en poudre fine ou bien dans un réacteur en lit fixe ou encore dans un réacteur tournant du type four à ciment avec le réactif solide en forme de granulé poreux.

Le procédé est de préférence mis en œuvre en semi-continu dans un ou plusieurs réacteurs tubulaires en lit fixe fonctionnant alternativement , par exemple selon la technologie du traitement des gaz par des tamis moléculaires. Après réaction le réactif solide partiellement ou totalement transformé en fluorure de calcium est déchargé du réacteur. Le fluorure de calcium, après éventuelle séparation de l'hydroxyde de calcium non réagi, peut être utilisé comme matière première dans la fabrication d'acide fluorhydrique.

Le procédé selon la présente invention peut comprendre le recyclage des réactifs non réagis à l'étape de déhydrofluoration.

PARTIE EXPERIMENTALE

Exemple 1

Dans un réacteur tubulaire de 850 mm de long et de 43 mm de diamètre chauffé à 140 ° C par une résistance électrique, on charge 500 g de chaux sodée SIGMA ALDRICH de granulométrie 0,15mm. On fait traverser le réacteur par un courant gazeux de 0,41 mole / h de HFC-236ea et 0,2 mole/h d'un gaz inerte.

Les gaz sortant du réacteur traversent un réfrigérant à 10° C pour éliminer la vapeur d'eau puis sont condensés dans un piège cryogénique. Après 80 min de fonctionnement en continu, la conversion globale du HFC-236ea est de 98 % et la sélectivité globale en HFO-1225ye est de 99 %.

Exemple 2

Dans le même appareillage que l'exemple 1 , on charge 575 g de chaux sodée SODASORB 4-8 REG HP (société GRACE),granulométrie 3-6 mm et dont la teneur en humidité est de 14-19 % en poids .

Le débit de réactif à l'entrée du réacteur est de 0,49 mole/h HFC-236ea et 0,17mole/h d'un gaz inerte.

Le tube est chauffé à 135° C et les gaz sortant du tube sont analysés et recueillis dans un piège cryogénique.

On observe une conversion de 100% de HFC-236ea pendant les 100 min de fonctionnement.

La sélectivité en HFO-1225ye est supérieure à 99 %

Exemple 3

Dans le même appareillage que l'exemple 1, on charge 690 g de chaux sodée SODASORB 4-8 REG HP (société GRACE,granulométrie 3-6 mm et dont la teneur en humidité est de 14-19 % en poids.

On chauffe le tube à 120° C et on introduit un débit de 0,5 mole/h de HFC245eb.

Les gaz sortant du tube sont analysés et recueillis dans un piège cryogénique

Après 4 h 35 de fonctionnement en continu, la conversion de HFC-245eb est de 100% et la sélectivité en 1234yf est de 99 %.

REVENDICATIONS

1) Procédé de fabrication continu ou semi-continu d'un composé (hydro)fluorooléfinique comprenant (i) la mise en contact d'au moins un composé comprenant de deux à six atomes de carbone, d'au moins deux atomes de fluor et d'au moins un atome d'hydrogène, à la condition qu' au moins un atome d'hydrogène et un atome de fluor sont situés sur des atomes de carbone adjacent, avec un réactif solide comprenant de l'hydroxyde de calcium.

2) Procédé selon la revendication 1 caractérisé en ce que le composé (hydro)fluorooléfinique de formule (I)

$$CF_3CY=CX_nH_p \qquad (I)$$

dans laquelle Y représente un atome d'hydrogène ou d'halogène choisi parmi le fluor, le chlore, le brome ou l'iode et X représente un atome d'halogène choisi parmi le fluor, le chlore, le brome ou l'iode ; n et p sont des nombres entiers et peuvent indépendamment prendre la valeur zéro, 1 ou 2 à condition que (n + p) = 2, comprenant la mise en contact d' un composé de formule $CF_3CYRCR'X_nH_p$, dans laquelle X, Y, n et p ont la même signification que dans la formule (I) et R représente un atome de fluor lorsque R' représente un atome d'hydrogène ou R représente un atome d'hydrogène lorsque R' représente un atome de fluor, avec un réactif solide comprenant de l'hydroxyde de calcium.

3) Procédé selon la revendication 1 caractérisé en ce que le composé (hydro)fluorooléfinique est de formule (Ia)

$$CF_3\text{-}CF=CHZ \qquad (Ia)$$

dans laquelle Z représente un atome d'hydrogène ou fluor comprend la mise en contact d'un composé de formule $CF_3CFRCHR'Z$, dans laquelle Z a la même signification que dans la formule (Ia) et R représente un atome de fluor lorsque R' représente un atome d'hydrogène ou R représente un atome d'hydrogène lorsque R' représente un atome de fluor, avec un réactif solide comprenant de l'hydroxyde de calcium solide.

4) Procédé selon l'une quelconque des revendications précédentes caractérisée en ce que le 2,3,3,3-tetrafluoropropène est obtenu par la mise en contact du 1,2,3,3,3-pentafluoropropane avec un réactif solide comprenant de l'hydroxyde de calcium et/ou le 1,2,3,3,3-pentafluoropropène par la mise en contact du 1,1,1,2,3,3-hexafluoropropane avec un réactif solide comprenant de l'hydroxyde de calcium.

5) Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que le réactif solide comprend entre 0,1 et 5 % en poids de KOH .

6) Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que le réactif solide comprend entre 0,1 et 5 % en poids de NaOH

7) Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que le taux d'humidité du réactif solide est compris entre 1 à 20 % en poids.

8) Procédé selon l'une quelconque des revendications précédentes caractérisé en ce qu'il est mis en œuvre à une température comprise entre 100 et 170 ° C.

9) Procédé selon l'une quelconque des revendications précédentes caractérisé en ce qu'il est mis en œuvre à une pression comprise entre 1 et 10 bar absolu.

10) Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que le réactif solide est sous forme de granulés de 1 à 10 mm .

INTERNATIONAL SEARCH REPORT

International application No
PCT/FR2010/050847

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C17/25 C07C21/18
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 practical, search terms used)
EPO-Internal, WPI Data, BEILSTEIN 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 2008/075017 A (INEOS FLUOR HOLDINGS LTD [GB]; SHARRATT ANDREW PAUL [GB]; LOW ROBERT E) 26 June 2008 (2008-06-26) cited in the application page 4, line 3 page 4, line 22 - line 25 page 5, paragraph 3 claims 1,7; examples 15,21; tables 2,4	1-10
X	US 3 499 048 A (REGAN BERNARD M) 3 March 1970 (1970-03-03) claims; examples	1-10
X	US 3 579 595 A (REGAN BERNARD M) 18 May 1971 (1971-05-18) claims; examples	1-10

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[X] Further documents are listed in the continuation of Box C.

[X] 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 document but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 September 2010	06/10/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Bedel, Christian

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/FR2010/050847

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 974 571 A (ATOCHEM NORTH AMERICA ELF [US] ATOFINA CHEM INC [US]) 26 January 2000 (2000-01-26) the whole document	1-10

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FR2010/050847

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008075017 A	26-06-2008	AU 2007336066 A1	26-06-2008
		CA 2673585 A1	26-06-2008
		CN 101563308 A	21-10-2009
		EP 2121548 A2	25-11-2009
		JP 2010513437 T	30-04-2010
		KR 20090090351 A	25-08-2009
		US 2010145111 A1	10-06-2010
US 3499048 A	03-03-1970	NONE	
US 3579595 A	18-05-1971	NONE	
EP 0974571 A	26-01-2000	AT 238258 T	15-05-2003
		DE 69907085 D1	28-05-2003
		DE 69907085 T2	04-12-2003
		DK 974571 T3	11-08-2003
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		JP 2000063300 A	29-02-2000
		PT 974571 E	31-07-2003
		US 6124510 A	26-09-2000

RAPPORT DE RECHERCHE INTERNATIONALE

Demande internationale n°
PCT/FR2010/050847

A. CLASSEMENT DE L'OBJET DE LA DEMANDE
INV. C07C17/25 C07C21/18
ADD.

Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB

B. DOMAINES SUR LESQUELS LA RECHERCHE A PORTE

Documentation minimale consultée (système de classification suivi des symboles de classement)
C07C

Documentation consultée autre que la documentation minimale dans la mesure où ces documents relèvent des domaines sur lesquels a porté la recherche

Base de données électronique consultée au cours de la recherche internationale (nom de la base de données, et si cela est réalisable, termes de recherche utilisés)
EPO-Internal, WPI Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie*	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
X	WO 2008/075017 A (INEOS FLUOR HOLDINGS LTD [GB]; SHARRATT ANDREW PAUL [GB]; LOW ROBERT E) 26 juin 2008 (2008-06-26) cité dans la demande page 4, ligne 3 page 4, ligne 22 - ligne 25 page 5, alinéa 3 revendications 1,7; exemples 15,21; tableaux 2,4	1-10
X	US 3 499 048 A (REGAN BERNARD M) 3 mars 1970 (1970-03-03) revendications; exemples	1-10
X	US 3 579 595 A (REGAN BERNARD M) 18 mai 1971 (1971-05-18) revendications; exemples	1-10

-/--

[X] Voir la suite du cadre C pour la fin de la liste des documents

[X] Les documents de familles de brevets sont indiqués en annexe

* Catégories spéciales de documents cités:

"A" document définissant l'état général de la technique, non considéré comme particulièrement pertinent

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"L" document pouvant jeter un doute sur une revendication de priorité ou cité pour déterminer la date de publication d'une autre citation ou pour une raison spéciale (telle qu'indiquée)

"O" document se référant à une divulgation orale, à un usage, à une exposition ou tous autres moyens

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"T" document ultérieur publié après la date de dépôt international ou la date de priorité et n'appartenenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention

"X" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive par rapport au document considéré isolément

"Y" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est associé à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier

"&" document qui fait partie de la même famille de brevets

Date à laquelle la recherche internationale a été effectivement achevée	Date d'expédition du présent rapport de recherche internationale
22 septembre 2010	06/10/2010

Nom et adresse postale de l'administration chargée de la recherche internationale	Fonctionnaire autorisé
Office Européen des Brevets, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Bedel, Christian

Formulaire PCT/ISA/210 (deuxième feuille) (avril 2005)

RAPPORT DE RECHERCHE INTERNATIONALE

Demande internationale n°
PCT/FR2010/050847

C(suite). DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie*	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
A	EP 0 974 571 A (ATOCHEM NORTH AMERICA ELF [US] ATOFINA CHEM INC [US]) 26 janvier 2000 (2000-01-26) le document en entier -----	1-10

RAPPORT DE RECHERCHE INTERNATIONALE

Renseignements relatifs aux membres de familles de brevets

Demande internationale n°
PCT/FR2010/050847

Document brevet cité au rapport de recherche	Date de publication	Membre(s) de la famille de brevet(s)	Date de publication
WO 2008075017 A	26-06-2008	AU 2007336066 A1	26-06-2008
		CA 2673585 A1	26-06-2008
		CN 101563308 A	21-10-2009
		EP 2121548 A2	25-11-2009
		JP 2010513437 T	30-04-2010
		KR 20090090351 A	25-08-2009
		US 2010145111 A1	10-06-2010
US 3499048 A	03-03-1970	AUCUN	
US 3579595 A	18-05-1971	AUCUN	
EP 0974571 A	26-01-2000	AT 238258 T	15-05-2003
		DE 69907085 D1	28-05-2003
		DE 69907085 T2	04-12-2003
		DK 974571 T3	11-08-2003
		ES 2195520 T3	01-12-2003
		JP 2000063300 A	29-02-2000
		PT 974571 E	31-07-2003
		US 6124510 A	26-09-2000

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATIONEN MATIÈRE DE BREVETS (PCT)

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(25) Langue de dépôt : français

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(30) Données relatives à la priorité :
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(71) Déposant *(pour tous les États désignés sauf US)* : **ARKEMA FRANCE** [FR/FR]; 420, rue d'Estienne d'Orves, F-92700 Colombes (FR).

(72) Inventeurs; et

(75) Inventeurs/Déposants *(pour US seulement)* : **PIGAMO, Anne** [FR/FR]; 9, rue de la Chapelle de Bel Air, F-69340 Francheville (FR). **DEVIC, Michel** [FR/FR]; 22, rue Georges Clémenceau, F-69110 Sainte Foy Les Lyon (FR). **WENDLINGER, Laurent** [FR/FR]; 18, hameau des Pierre Blanches, F-69510 Soucieu En Jarrest (FR).

(74) Mandataire : **DANG, Doris**; Arkema France, Departement Propriete Industrielle, 420, rue d'Estienne d'Orves, F-92705 Colombes Cedex (FR).

(81) États désignés *(sauf indication contraire, pour tout titre de protection nationale disponible)* : AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) États désignés *(sauf indication contraire, pour tout titre de protection régionale disponible)* : ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), eurasien (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), européen (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Déclarations en vertu de la règle 4.17 :

— *relative au droit du déposant de demander et d'obtenir un brevet (règle 4.17.ii))*

Publiée :

— *avec rapport de recherche internationale (Art. 21(3))*

— *avant l'expiration du délai prévu pour la modification des revendications, sera republiée si des modifications sont reçues (règle 48.2.h))*

WO 2010/029239 A1

(54) **Title** : PROCESS FOR THE PREPARATION OF FLUOROOLEFIN COMPOUNDS

(54) **Titre** : PROCEDE DE PREPARATION DE COMPOSES FLUORES OLEFINIQUES

(57) **Abstract** : One subject of the invention is a process for the preparation of fluoroolefin compounds. It relates more particularly to a process for the manufacture of a compound of formula (I) CF_3-CF=CHX in which X represents a hydrogen or fluorine atom, comprising at least one stage of dehydrofluorination of a compound of formula (II) CF_3-CHF-CHFX, during which the compound of formula (II) is brought into contact with a mixture composed of water and potassium hydroxide in which the potassium hydroxide is present in an amount of between 58 and 86% by weight.

(57) **Abrégé** : L'invention a pour objet un procédé de préparation de composés fluorés oléfiniques. Elle concerne plus particulièrement un procédé de fabrication d'un composé de formule (I) CF_3-CF=CHX dans lequel X représente un atome d'hydrogène ou fluor, comprenant au moins une étape de déhydrofluoration d'un composé de formule (II) CF_3-CHF-CHFX, au cours de laquelle ou desquelles le composé de formule (II) est mis en contact avec un mélange constitué d'eau et d'hydroxyde de potassium, dans lequel l'hydroxyde de potassium est présent en quantité comprise en 58 et 86 % en poids.

PROCEDE DE PREPARATION DE COMPOSES FLUORES OLEFINIQUES

DOMAINE DE L'INVENTION

L'invention a pour objet un procédé de préparation de composés fluorés oléfiniques. Elle concerne plus particulièrement un procédé de préparation de 1,2,3,3,3-pentafluoropropène (HFO-1225ye) et de 2,3,3,3-tétrafluoro-1-propène (HFO-1234yf).

ARRIERE-PLAN TECHNOLOGIQUE

Les hydrofluorocarbones (HFC) et en particulier les hydrofluorooléfines (HFOs), telles que le 2,3,3,3-tétrafluoro-1-propène (HFO-1234yf) sont des composés connus pour leurs propriétés de réfrigérants et fluides caloporteurs, extinctrices, propulseurs, agents moussants, agents gonflants, diélectriques gazeux, milieu de polymérisation ou monomère, fluides supports, agents pour abrasifs, agents de séchage et fluides pour unité de production d'énergie. A la différence des CFC et des HCFC, qui sont potentiellement dangereux pour la couche d'ozone, les HFOs ne contiennent pas de chlore et donc ne posent pas de problème pour la couche d'ozone.

Le 1,2,3,3,3- pentafluoropropène (HFO-1225ye) est un intermédiaire de synthèse dans la fabrication du 2,3,3,3-tétrafluoro-1-propène (HFO-1234yf).

La plupart des procédés de fabrication des hydrofluorooléfines font appel à une réaction de déhydrohalogénation. Ainsi, le document WO 03/027051 décrit un procédé de fabrication de fluorooléfines de formule $CF_3CY=CX_nH_p$, dans laquelle X représente un atome d'hydrogène ou d'halogène choisi parmi le fluor, le chlore, le brome ou l'iode ; n et p sont des nombres entiers et peuvent indépendamment prendre la valeur zéro, 1 ou 2 à condition que (n + p) = 2, comprenant la mise en contact d'un composé de formule $CF_3C(R^1_aR^2_b)C(R^3_cR^4_d)$ avec R^1, R^2, R^3 et R^4 représentant indépendamment un atome d'hydrogène ou d'halogène choisi parmi le fluor, le chlore, le brome ou l'iode à condition qu'au moins un de R^1, R^2, R^3 et R^4 est un atome d'halogène et qu'au moins un atome d'hydrogène et un atome d'halogène sont situés sur des atomes de carbone adjacent ; a et b peuvent indépendamment prendre la valeur zéro, 1 ou 2 à condition que (a + b) = 2 ; c et d peuvent indépendamment prendre la valeur zéro, 1, 2 ou 3 à condition que (c + d) = 3, avec au moins un hydroxyde de métal alcalin en présence d'un catalyseur de transfert phase.

Ce document enseigne à l'exemple 2, qu'en l'absence d'un catalyseur de transfert de phase, il n'y a pas de réaction lorsque le 1,1,1,3,3-pentafluoropropane

(HFC-245fa) est mis en contact avec une solution aqueuse de 50 % en poids de hydroxyde de potassium (KOH) pendant 24 heures à température ambiante et sous pression.

Ce document enseigne en outre une température de réaction compris entre –20°C et 80°C.

Le document WO 2008/075017 illustre la réaction de déhydrofluoration du 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) en 1,2,3,3,3-pentafluoropropène (HFO-1225ye) à 150°C en présence d'une solution aqueuse de 50 % en poids de KOH. En l'absence d'un catalyseur de transfert de phase, la conversion au bout de 3 heures et demie est de 57,8 % et la sélectivité en HFO-1225ye est de 52,4 % (essai 1). En présence d'un catalyseur de transfert de phase, cette conversion est atteinte au bout de 2,5 heures seulement et la sélectivité est pratiquement inchangée (essai 4). Comme indiqué au tableau 2 de ce document pour accroître la sélectivité en HFO-1225ye, il est nécessaire d'utiliser un solvant organique.

WO 2007/056194 décrit la préparation de HFO-1234yf par déhydrofluoration du 1,1,1,2,3-pentafluoropropane (HFC-245eb) soit avec une solution aqueuse de KOH soit en phase gazeuse en présence d'un catalyseur, notamment sur catalyseur à base de nickel, de carbone ou une combinaison de ceux-ci.

Le document Knunyants et al, Journal of the USSR Academy of Sciences, Chemistry Department, "reactions of fluoro-olefins", report 13., "catalytic hydrogenation of perfluoro-olefins", 1960, décrit de façon distincte diverses réactions chimiques sur des composes fluorés. Ce document décrit la déhydrofluoration du 1,1,1,2,3,3-hexafluoropropane (236ca) par passage au travers d'une suspension de KOH en poudre dans l'éther de dibutyle, pour produire du 1,2,3,3,3-pentafluoropropène-1 (HFO-1225ye) avec un rendement de 60 % seulement. Ce document décrit également la déhydrofluoration de 1,1,1,2,3-pentafluoropropane (HFC-245eb) en 2,3,3,3-tétrafluoro-1-propène (HFO-1234yf) par passage dans une suspension de KOH en poudre dans l'éther de dibutyle avec un rendement de 70 % seulement.

Par ailleurs, la figure 2 à la page 51 du deuxième fascicule du nouveau traité de chimie minérale de P. Pascal, Ed. 1963, montre l'allure des équilibres liquide solide du système eau et hydroxyde de potassium et les mesures sont rassemblées dans le tableau à la page 52.

Il a maintenant été trouvé un procédé de fabrication d'un composé de formule (I) CF_3-CF=CHX dans lequel X représente un atome d'hydrogène ou fluor, comprenant au moins une étape de déhydrofluoration d'un composé de formule (II) CF_3-CHF-CHFX, avec une très bonne sélectivité et/ou rendement élevé.

La présente invention a donc pour objet un procédé de fabrication d'un composé de formule (I) CF_3-CF=CHX dans lequel X représente un atome d'hydrogène ou fluor, comprenant au moins une étape de déhydrofluoration d'un composé de formule (II) CF_3-CHF-CHFX, au cours de laquelle ou desquelles le composé de formule (II) est mis en contact avec un mélange constitué d'eau et d'hydroxyde de potassium, dans lequel l'hydroxyde de potassium est présent en quantité comprise entre 58 et 86 % en poids de préférence comprise entre 58 et 69 % en poids et avantageusement comprise entre 60 et 66 % en poids, ledit mélange étant maintenu à une température comprise entre 125 et 180°C.

De préférence, la température du mélange eau et hydroxyde est comprise entre 145 et 180°C, et avantageusement entre 152 et 165°C.

Selon un mode de réalisation de l'invention, le mélange d'eau et d'hydroxyde peut être obtenu à partir des hydrates de formule KOH. x H_2O , x étant compris entre 1 et 2 inclus.

L'étape de déhydrofluoration peut être mise en œuvre dans tout type de réacteur connu de l'homme de l'art. On peut utiliser, un réacteur agité, un mélangeur statique, une colonne réactive, une tuyère ou tout simplement faire buller le composé de formule (II) dans ledit mélange d'eau et d'hydroxyde de potassium contenu dans un récipient.

Outre les étapes de déhydrofluoration, le procédé comprend une étape de séparation du composé de formule (I) suivie éventuellement d'une étape de purification.

On peut opérer de façon continue, semi continue, ou discontinue à pression atmosphérique ou sous pression, de préférence inférieure à 2 bars absolus.

La demanderesse a observé que la vitesse de déhydrofluoration du composé de formule (II) est très élevée avec le mélange d'eau et d'hydroxyde tel que décrit précédemment et donc particulièrement intéressante pour mettre en œuvre le procédé, selon la présente invention, en continu.

Selon un mode de réalisation préféré de l'invention, on introduit en continu le composé de formule (II) et le mélange constitué d'eau et d'hydroxyde tel que défini

précédemment dans un réacteur, initialement chargé de ce mélange, maintenu à la température précitée et on soutire en continu de la phase gaz du réacteur un flux comprenant le composé de formule (I). Le fluorure de potassium formé comme sous produit peut être soutiré de façon continue ou discontinue du milieu réactionnel liquide par exemple par filtration. La concentration en eau du milieu réactionnel peut être maintenue constante par évaporation en continu de l'eau formée par la réaction.

Lorsqu'on opère en discontinu ou semi-continu, le ratio molaire KOH / composé de formule (II) mis en jeu, est en général compris entre 2 et 100, de préférence compris entre 3 et 20.

Le procédé convient tout particulièrement à la fabrication du 2,3,3,3-tetrafluoropropène par déhydrofluoration du 1,2,3,3,3-pentafluoropropane.

Il convient également à la fabrication du 1,2,3,3,3-pentafluoropropène par déhydrofluoration du 1,1,1,2,3,3-hexafluoropropane. Le 1,2,3,3,3-pentafluoropropène peut être sous la forme d'isomère Z et/ou E.

La demanderesse a découvert que le sous produit trifluorure de vinyle peut être réduit dans le cas de la déhydrofluoration du HFC-236ea. Ce sous-produit devient négligeable, lorsque la température de déhydrofluoration est comprise entre 125 et 145 °C et le KOH est présent entre 58 et 69 % en poids, de préférence entre 60 et 66 % en poids dans le mélange eau-KOH.

Il peut être avantageux d'utiliser un gaz inerte, de préférence de l'azote ou de l'hydrogene dans l'étape de déhydofluoration.

Selon la conversion recherchée, la réaction de déhydrohalogénation peut être mise en œuvre en plusieurs étapes, éventuellement à l'aide de plusieurs réacteurs en série, de préférence en deux étapes, éventuellement à l'aide de deux réacteurs en série.

Le procédé selon la présente invention a l'avantage de conduire à des rendements élevés même en l'absence de catalyseur de transfert de phase et/ou de solvant organique.

PARTIE EXPERIMENTALE

La conversion est définie comme le pourcentage du composé de formule (II) ayant réagi (nombre de moles de composé de formule (II) réagi / nombre de moles de composé de formule (II) introduit).

La sélectivité est définie comme le pourcentage du ratio du nombre de moles de composé de formule (I) ou sous-produit formé / nombre de moles de composé de formule (II) ayant réagi.

Le rendement est défini comme pourcentage du ratio du nombre de moles de composé de formule (I) ou sous-produit formé / nombre de moles de composé de formule (II) introduit.

Exemple 1

Dans un réacteur cylindrique d'un litre, en acier inox, équipé d'un dispositif de chauffage et de mesure de température du milieu réactionnel, on introduit 1005 g d'un mélange eau et KOH dans lequel le KOH est présent à 66 % en poids. A l'aide d'un tube plongeur, on fait buller dans le milieu maintenu à 135°C du HFC-236ea avec un débit de 150 g/h et de l'hydrogène avec un débit de 12 Nl/h. Les produits gazeux sortent du réacteur par un orifice situé sur le couvercle et sont séchés par une colonne de tamis moléculaire, puis recueillis dans un piège en acier inox refroidi par de l'azote liquide.
On arrête la réaction après introduction de 48,3 g de HFC-236ea et on obtient :

- une conversion de 92,7 % en HFC-236ea
- une sélectivité de 99 % en HFO-1225ye (E + Z)
- un rendement de 89,9 % en HFO-1225yeE.

La concentration molaire du CF_2=CFH dans le liquide recueilli dans le piège à la sortie du réacteur est de 0,02 % .

Exemple 2

On utilise deux réacteurs en série, du même type que celui de l'exemple 1 à l'exception du premier réacteur qui a un volume de 4 litres, le flux gazeux issu du premier réacteur alimente le deuxième réacteur. On introduit dans le premier réacteur 4380 g d'un mélange d'eau-KOH avec le KOH présent à 66 % en poids et dans le deuxième réacteur 1200 g d'un mélange d'eau-KOH avec le KOH présent à 70 % en poids, la température du milieu est maintenue à 160°C. On introduit du HFC-236ea dans le premier réacteur avec un débit de 165 g/h et on arrête la réaction après introduction de 1100 g de HFC-236ea dans le premier réacteur.

On obtient une conversion de 99,3 % de HFC-236ea, une sélectivité en 1225ye (E+Z) de 98 %. La concentration molaire du CF_2=CFH dans le liquide recueilli dans le piège à la sortie du réacteur est de 0,19 %.

Exemple 3

On opère avec l'appareillage de l'exemple 1. On introduit dans le réacteur 1055 g d'un mélange eau et KOH dans lequel le KOH est présent à 86 % en poids. On introduit dans le milieu maintenu à 165°C, du HFC-236ca avec un débit de 150 g/h et on arrête la réaction après introduction de 1000 g de HFC-236ea.

On obtient une conversion de 98,2 % de HFC-236ea, une sélectivité en HFO-1225ye (E+Z) de 95 %. La concentration molaire du CF_2=CFH dans le liquide recueilli dans le piège à la sortie du réacteur est de 1 %.

Exemple 4

On opère avec l'appareillage de l'exemple 1. On introduit dans le réacteur 1000 g d'un mélange d'eau et KOH, le KOH étant présent à 75 % en poids. On introduit dans le milieu maintenu à 160°C, du HFC-245eb avec un débit de 150 g/h et on arrête la réaction après introduction de 276 g de HFC-245eb.

On obtient une conversion de 83,2 % de HFC-245eb, une sélectivité de 99 % en HFO-1234yf. La concentration molaire de tetrafluoropropane dans le liquide recueilli dans le piège à la sortie du réacteur est de 1,5 %.

REVENDICATIONS

1. Procédé de fabrication d'un composé de formule (I) CF_3-CF=CHX, dans lequel X représente un atome d'hydrogène ou fluor, comprenant au moins une étape de déhydrofluoration d'un composé de formule (II) CF_3-CHF-CHFX, au cours de laquelle ou desquelles le composé de formule (II) est mis en contact avec un mélange constitué d'eau et d'hydroxyde de potassium, dans lequel l'hydroxyde de potassium est présent en quantité comprise en 58 et 86 % en poids, de préférence comprise entre 58 et 69 % en poids et avantageusement comprise entre 60 et 66 % en poids, ledit mélange étant maintenu à une température comprise entre 125 et 180°C.
2. Procédé selon la revendication 1 caractérisé en ce que X dans les formules (I) et (II) représente un atome d'hydrogène.
3. Procédé selon la revendication 1 caractérisé en ce que X dans les formules (I) et (II) représente un atome de fluor.
4. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que l'on opère en continu.
5. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce qu'il comprend au moins deux étapes de déhydrofluoration.
6. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que l'on opère en l'absence de solvant organique et/ou catalyseur de transfert de phase.
7. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que le mélange eau et hydroxyde est obtenu à partir des hydrates de formule KOH. x H_2O, x étant compris entre 1 et 2 inclus.
8. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce qu'il comprend une étape de séparation du composé de formule (I) et éventuellement une étape de purification.
9. Procédé selon l'une quelconque des revendications précédentes caractérisé en ce que la température du mélange est comprise entre 145 et 180°C, de préférence entre 152 et 165°C.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FR2009/051594

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C17/25 C07C21/18

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 practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SIANESI DARIO ET AL: "Fluoro olefins. I. cis- and trans-1,2,3,3,3-Pentafluoropropylene" ANNALI DI CHIMICA, SOCIETA CHIMICA ITALIANA, ROME, IT, vol. 55, no. 8-9, 1 January 1965 (1965-01-01), pages 850-861, XP009092725 ISSN: 0003-4592	1,3-4,6, 8-9
Y	page 853, paragraphs 6,7 page 859, paragraph 5	2,5,7

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[X] 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 document but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 February 2010	10/02/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Delanghe, Patrick

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KNUNYANTS I L ET AL: "REACTIONS OF FLUORO OLEFINS. ÖCOMMUNICATION 13. CATALYTIC HYDROGENATION OF PERFLUORO OLEFINS" BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR, DIVISION OFCHEMICAL SCIENCES,, 1 January 1960 (1960-01-01), pages 1312-1317, XP000578879 ISSN: 0568-5230 cited in the application page 1316, paragraphs 2,4	2,5,7

RAPPORT DE RECHERCHE INTERNATIONALE

Demande internationale n°
PCT/FR2009/051594

A. CLASSEMENT DE L'OBJET DE LA DEMANDE
INV. C07C17/25 C07C21/18

Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB

B. DOMAINES SUR LESQUELS LA RECHERCHE A PORTE

Documentation minimale consultée (système de classification suivi des symboles de classement)
C07C

Documentation consultée autre que la documentation minimale dans la mesure où ces documents relèvent des domaines sur lesquels a porté la recherche

Base de données électronique consultée au cours de la recherche internationale (nom de la base de données, et si cela est réalisable, termes de recherche utilisés)
EPO-Internal

C. DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie*	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
X	SIANESI DARIO ET AL: "Fluoro olefins. I. cis- and trans-1,2,3,3,3-Pentafluoropropylene" ANNALI DI CHIMICA, SOCIETA CHIMICA ITALIANA, ROME, IT, vol. 55, no. 8-9, 1 janvier 1965 (1965-01-01), pages 850-861, XP009092725 ISSN: 0003-4592	1,3-4,6, 8-9
Y	page 853, alinéas 6,7 page 859, alinéa 5	2,5,7

-/--

[X] Voir la suite du cadre C pour la fin de la liste des documents

[ ] Les documents de familles de brevets sont indiqués en annexe

* Catégories spéciales de documents cités:

"A" document définissant l'état général de la technique, non considéré comme particulièrement pertinent

"E" document antérieur, mais publié à la date de dépôt international ou après cette date

"L" document pouvant jeter un doute sur une revendication de priorité ou cité pour déterminer la date de publication d'une autre citation ou pour une raison spéciale (telle qu'indiquée)

"O" document se référant à une divulgation orale, à un usage, à une exposition ou tous autres moyens

"P" document publié avant la date de dépôt international, mais postérieurement à la date de priorité revendiquée

"T" document ultérieur publié après la date de dépôt international ou la date de priorité et n'appartenenant pas à l'état de la technique pertinent, mais cité pour comprendre le principe ou la théorie constituant la base de l'invention

"X" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme nouvelle ou comme impliquant une activité inventive par rapport au document considéré isolément

"Y" document particulièrement pertinent; l'invention revendiquée ne peut être considérée comme impliquant une activité inventive lorsque le document est associé à un ou plusieurs autres documents de même nature, cette combinaison étant évidente pour une personne du métier

"&" document qui fait partie de la même famille de brevets

Date à laquelle la recherche internationale a été effectivement achevée	Date d'expédition du présent rapport de recherche internationale
4 février 2010	10/02/2010

Nom et adresse postale de l'administration chargée de la recherche internationale	Fonctionnaire autorisé
Office Européen des Brevets, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Delanghe, Patrick

Formulaire PCT/ISA/210 (deuxième feuille) (avril 2005)

C(suite). DOCUMENTS CONSIDERES COMME PERTINENTS

Catégorie*	Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents	no. des revendications visées
Y	KNUNYANTS I L ET AL: "REACTIONS OF FLUORO OLEFINS. ÖCOMMUNICATION 13. CATALYTIC HYDROGENATION OF PERFLUORO OLEFINS" BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR, DIVISION OFCHEMICAL SCIENCES,, 1 janvier 1960 (1960-01-01), pages 1312-1317, XP000578879 ISSN: 0568-5230 cité dans la demande page 1316, alinéas 2,4	2,5,7

Espacenet

Bibliographic data: FR 2935702 (A1)

Preparing pentafluoropropene, useful as intermediate for synthesizing tetrafluoropropene, comprises dehydrofluorinating hexafluoropropane, and contacting hexafluoropropane with mixture comprising water and potassium hydroxide

Publication date:	2010-03-12
Inventor(s):	PIGAMO ANNE [FR]; DEVIC MICHEL [FR]; WENDLINGER LAURENT [FR] +
Applicant(s):	ARKEMA FRANCE [FR] +
Classification:	**- international:** ***C07C17/25; C07C21/18***
	- European: C07C17/25
Application number:	FR20090056313 20090915
Priority number(s):	FR20090056313 20090915
Also published as:	• FR 2935702 (B1)

Abstract of FR 2935702 (A1)

Preparing 1,2,3,3,3-pentafluoropropene (I) comprises: dehydrofluorinating 1,1,1,2,3,3-hexafluoropropane (II); and contacting (II) with a mixture comprising water and potassium hydroxide, where the: potassium hydroxide is present at 58-69 wt.%, preferably 60-66 wt.%; and mixture is maintained at 125-160[deg] C.

Last updated: 12.10.2011 Worldwide Database 5.7.23.2; 93p

Electronic Acknowledgement Receipt

EFS ID:	11304069
Application Number:	13229016
International Application Number:	
Confirmation Number:	8706
Title of Invention:	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS
First Named Inventor/Applicant Name:	SELMA BEKTESEVIC
Customer Number:	91970
Filer:	John Eric Sumner/Michele Greenberg
Filer Authorized By:	John Eric Sumner
Attorney Docket Number:	H0024680-4511
Receipt Date:	31-OCT-2011
Filing Date:	09-SEP-2011
Time Stamp:	17:18:02
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	int1B7B.PDF	614048 c2f50ca00854d92d31adc62049f728b9a5507b36	no	7

Warnings:	
Information:	

2	Foreign Reference	int1B7C.PDF	658673 937d53970ceede0c352b404556ad73bfc1c58755	no	18
Warnings:					
Information:					
3	Foreign Reference	int1B7D.PDF	1115040 d8a861059b585bdee6fc8d846bf4583f5dd3a3c8	no	14
Warnings:					
Information:					
4	Foreign Reference	int1B7E.PDF	856825 0fcbb9a74f80d212e9b62f765ebfb12dcd9a176e	no	19
Warnings:					
Information:					
5	Foreign Reference	int1B7F.PDF	56350 0c07b07c4a907e7068873538aeaf20362725a4c0	no	1
Warnings:					
Information:					
6	Foreign Reference	int1B80.PDF	546606 25ec6b6b30ad1bc8db969457416e74f1cdaed1e7	no	10
Warnings:					
Information:					
7	Foreign Reference	int1B81.PDF	1043948 7fef872fa7a83fb26d6995a278e86ea6ff8b9a2b	no	15
Warnings:					
Information:					
8	Foreign Reference	int1B82.PDF	226405 37bc2860dfd8f28903ce00fb7ba84039a2d6e6e5	no	8
Warnings:					
Information:					
9	Foreign Reference	int1B83.PDF	75941 33a8499ccd66fe1a51503720cb545a0b2e65c02d	no	4
Warnings:					
Information:					
10	Foreign Reference	int1B84.PDF	2529838 c14d95805457c93fb847129ac1ca20604bf45eaf	no	24
Warnings:					
Information:					

11	Foreign Reference	int1B85.PDF	1706809 0f990069a877959779c420d6f22f787a398052b7	no	15
Warnings:					
Information:					
12	Foreign Reference	int1B86.PDF	1473613 d9fdb10692737c2834f8db595cdfa0fed98f6b78	no	12
Warnings:					
Information:					
13	Foreign Reference	int1B87.PDF	28884 34284378882f6822117094ce076a3cdb3210bb40	no	1
Warnings:					
Information:					
14	Non Patent Literature	int1B88.PDF	294000 e27f1077afc989b5d338d590110efa37f782fc7e	no	5
Warnings:					
Information:					
15	Non Patent Literature	int1B89.PDF	240193 92be8c508b9aa9a64d1deaa46f3ba4e5e3b7b182	no	3
Warnings:					
Information:					
16	Non Patent Literature	int1BBF.PDF	305429 2e69c340b60fdfd3e17530870deb5e8add89ebcc	no	3
Warnings:					
Information:					
			Total Files Size (in bytes):	11772602	

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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.

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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
13/229,016	09/09/2011	SELMA BEKTESEVIC	H0024680-4511

CONFIRMATION NO. 8706

91970
HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962

PUBLICATION NOTICE

Title:INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS

Publication No.US-2012-0022302-A1
Publication Date:01/26/2012

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Office of Public Records. The Office of Public Records can be reached by telephone at (703) 308-9726 or (800) 972-6382, by facsimile at (703) 305-8759, by mail addressed to the United States Patent and Trademark Office, Office of Public Records, Alexandria, VA 22313-1450 or via the Internet.

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Approved for use through 07/31/2012. OMB 0651-0031
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	13229016
Filing Date	2011-09-09
First Named Inventor	Selma Bektesevic
Art Unit	1621
Examiner Name	Clinton A. Brooks
Attorney Docket Number	H0024680-4511

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2009/084703	WO	A1	2009-07-09	Daikin Ind Ltd et al.		☐
	2	2009/125201	WO	A2	2009-10-15	Ineos Fluor Holdings Liimited et al.		☐

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	13229016
Filing Date	2011-09-09
First Named Inventor	Selma Bektesevic
Art Unit	1621
Examiner Name	Clinton A. Brooks
Attorney Docket Number	H0024680-4511

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	PCT/US/2011/55198 Search Report, dated May 4, 2012.	☐

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EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	13229016
Filing Date	2011-09-09
First Named Inventor	Selma Bektesevic
Art Unit	1621
Examiner Name	Clinton A. Brooks
Attorney Docket Number	H0024680-4511

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☒ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☐ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/J. Eric Sumner/	Date (YYYY-MM-DD)	2012-07-31
Name/Print	J. Eric Sumner	Registration Number	58699

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

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5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Docket No.: H0024680-4511
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Selma Bektesevic et al.

Application No.: 13/229,016 Confirmation No.: 8706

Filed: September 9, 2011 Art Unit: 1621

For: Integrated Continuous Process For Dehydrofluorination of 236ea and 245eb Examiner: Clinton A. Brooks

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT (IDS)

MS Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Madam:

In accordance with 37 CFR 1.97, Applicant(s) hereby make of record the following additional documents. A PTO Form SB/08 and a full copy of each of the documents required under 37 CFR 1.98(a)(2) accompany this statement.

Applicant(s) have become aware of the following documents, cited in an International Search Report issued May 4, 2012, during the prosecution of International Application No. PCT/US11/55198, which corresponds to the above referenced application, and in accordance with 37 CFR 1.97(c) and (e)(1) or (b)(3), hereby submit(s) these documents for the Examiner's consideration. These documents are cited on the enclosed PTO Form SB/08, and a copy of the International Search Report and of each document required under 37 CFR 1.98(a)(2) cited thereon are enclosed as well.

This statement is not to be interpreted as a representation that the cited documents are material, that an exhaustive search has been conducted, or that no other relevant information exists. Nor shall the

citation of any document herein be construed *per se* as a representation that such document is prior art. Moreover, Applicant(s) understand(s) the Examiner will make an independent evaluation of the cited documents.

This Information Disclosure Statement is filed before the mailing date of a first Office Action on the merits as far as is known to the undersigned (37 CFR 1.97(b)(3)).

Furthermore, in accordance with 37 CFR 1.704(d), Applicant(s) note(s) that to our knowledge each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart application and that this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

The Director is hereby authorized to charge any deficiency in the fees filed, asserted to be filed or which should have been filed herewith (or with any paper hereafter filed in this application by this firm) to our Deposit Account No. 50-1943, under Order No. 039643.01561.

Dated: July 31, 2012

Respectfully submitted,

Electronic signature: /J. Eric Sumner/
J. Eric Sumner
Registration No.: 58,699
FOX ROTHSCHILD LLP
2000 Market Street
20th Floor
Philadelphia, Pennsylvania 19103-3222
(215) 299-2772
(215) 299-2150 (Fax)
Attorneys/Agents For Applicant

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference H0024680451I	FOR FURTHER ACTION	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
International application No. PCT/US2011/055198	International filing date *(day/month/year)* 07 OCTOBER 2011 (07.10.2011)	(Earliest) Priority Date *(day/month/year)* 12 OCTOBER 2010 (12.10.2010)

Applicant

HONEYWELL INTERNATIONAL INC. et al

This International search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 8 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the language, the international search was carried out on the basis of :
      ☒ the international application in the language in which it was filed
      ☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))
   b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).
   c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.
2. ☐ **Certain claims were found unsearchable** (See Box No. II)
3. ☐ **Unity of invention is lacking** (See Box No. III)
4. With regard to the **title**,
   ☒ the text is approved as submitted by the applicant.
   ☐ the text has been established by this Authority to read as follows:
5. With regard to the **abstract**,
   ☒ the text is approved as submitted by the applicant.
   ☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.
6. With regard to the drawings,
   a. the figure of the drawings to be published with the abstract is Figure No. 1
      ☒ as suggested by the applicant.
      ☐ as selected by this Authority, because the applicant failed to suggest a figure.
      ☐ as selected by this Authority, because this figure better characterizes the invention.
   b. ☐ none of the figure is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2011/055198

A. CLASSIFICATION OF SUBJECT MATTER

C07C 17/23(2006.01)i, C07C 21/18(2006.01)i, C07C 19/08(2006.01)i, C07C 17/38(2006.01)i

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 17/23; C07C 21/18; C07C 17/25; C07C 19/08; C07C 17/20; B01J 19/00; C07C 17/354

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: hydrogenat*, dehydrohalogenat*, reducing agent, recover*, recycl*, 236ea, 245eb, 1225ye, 1234yf.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009-0234165 A1 (CHIU, YUON et al.) 17 September 2009 See abstract; Figure 10; paragraphs [0024]-[0074]; claims 1-17.	1-11
A	US 2010-0029997 A1 (WANG, HAIYOU et al.) 04 February 2010 See abstract; paragraphs [0010], [0024]-[0028]; claims 9 & 12.	1-11
A	WO 2009-084703 A1 (DAIKIN INDUSTRIES, LTD.) 09 July 2009 See abstract; claims 1-2.	1-11
A	WO 2009-125201 A2 (INEOS FLUOR HOLDINGS LIMITED) 15 October 2009 See abstract; claims 1, 13-14 & 16-17.	1-11

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

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 APRIL 2012 (26.04.2012)	**04 MAY 2012 (04.05.2012)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 189 Cheongsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer KIM, Dongseok Telephone No. 82-42-481-8647

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2011/055198

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(71) Applicant *(for all designated States except US)*: **DAIKIN INDUSTRIES, LTD.** [JP/JP]; Umeda Center Building, 4-12, Nakazaki-Nishi 2-Chome, Kita-ku, Osaka-shi, Osaka, 5308323 (JP).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **TAKAHASHI, Kazuhiro** [JP/JP]; c/o Yodogawa Plant of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka, 5668585 (JP). **SHIBANUMA, Takashi** [JP/JP]; c/o Yodogawa Plant of DAIKIN INDUSTRIES, LTD., 1-1, Nishihitotsuya, Settsu-shi, Osaka, 5668585 (JP).

(74) Agents: **TANAKA, Mitsuo** et al.; AOYAMA & PARTNERS, IMP Building, 3-7, Shiromi 1-chome, Chuo-ku, Osaka-shi, Osaka, 5400001 (JP).

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(54) Title: PROCESS FOR PRODUCING 1,1,1,2-TETRAFLUOROPROPENE

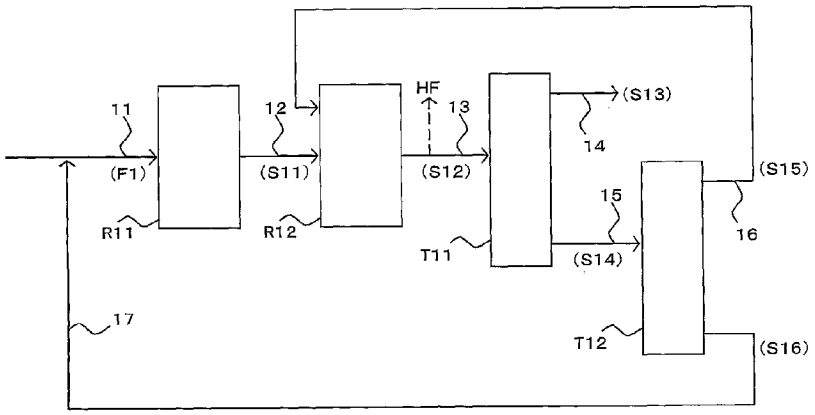

Fig. 1

(57) Abstract: Using hexafluoropropene (HFP) as a raw material, 1,1,1,2-tetrafluoropropene (HFC-1234yf) is obtained by hydrogenation, dehydrofluorination and distillation. In a series of reactions comprised of hydrogenating HFP to obtain 1,1,1,2,3,3-hexafluoropropane (HFC-236ca), dehydrofluorinating the HFC-236ca to obtain 1,1,1,2,3-pentafluoropropene (HFC-1225ye), hydrogenating the HFC-1225ye to obtain 1,1,1,2,3-pentafluoropropane (HFC-245eb), and dehydrofluorinating the HFC-245eb to obtain HFC-1234yf, the hydrogenations and the dehydrofluorinations are respectively carried out in the one step, and then distillation is carried out so that HFC-1234yf can be obtained. Alternately, HFC-1234yf can also be obtained by hydrogenating HFP to directly obtain HFC-245eb, and separating the HFC-245eb by distillation and dehydrofluorinating it. Thus, HFC-1234yf can be produced with a high selectivity.

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DESCRIPTION

PROCESS FOR PRODUCING 1,1,1,2-TETRAFLUOROPROPENE

Technical Field

The present invention relates to a process for producing 1,1,1,2-tetrafluoropropene.

Background Art

CFCs (chlorofluorocarbons) and HCFCs (hydrochlorofluorocarbons) were conventionally used as refrigerants. Since these substances can cause depletion of the ozone layer, HFCs (hydrofluorocarbons), particularly HFC-125 (pentafluoroethane) and HFC-32 (difluoromethane) have widely been used as substitute refrigerants. However, HFC-125 and HFC-32 are potent global warming substances and cause concern of diffusion of these substances to adversely affect the global warming. Although these substances are recovered from disused apparatuses for the purpose of preventing their diffusion and consequently the global warming, all of these substances cannot be recovered. Also, diffusion caused by leaking or the like cannot be neglected. Then, CO_2 and hydrocarbon compounds are studied to be used as other substitute refrigerants. However, the CO_2 refrigerant has poor efficiency and requires a larger

device, so that there are a lot of problems in reducing overall greenhouse gas emission including consumption energy of the device. Also, the hydrocarbon compounds have problems about safety due to their high combustibility.

Recently, intense interest has been shown towards, as a substitute refrigerant being able to solve these problems, 1,1,1,2-tetrafluoropropene (or 2,3,3,3-tetrafluoropropene, $CF_3CF=CH_2$, hereinafter also referred to as "HFC-1234yf"), which is a HFC of an olefin having a low warming coefficient.

Some processes for producing HFC-1234yf have hitherto been disclosed. Patent Document 1 listed below describes a process of using $CF_3CH=CH_2$ as a raw material, halogenating it and then subjecting to a dehydrofluorination reaction to obtain HFC-1234yf. Patent Document 2 listed below describes a process of hydrogenating a fluorinated olefin having 3 to 6 carbon atoms through at least two reaction stages to give an alkane, and dehydrofluorinating the alkane to produce a fluorinated olefin such as HFC-1234yf. Patent Document 3 listed below describes a process of directly obtaining HFC-1234yf from a mixture of $CF_3CF_2CHCl_2$ (HCFC-225ca) and $CClF_2CF_2CHClF$ (HCFC-225cb) using a Pd/C catalyst. Patent Document 4 listed below describes a process of coupling an alkane having 1 carbon atom with an alkane having 2 carbon atoms to produce an olefin having 3

carbon atoms such as HFC-1234yf. Patent Document 5 listed below describes a process of synthesizing an alkane having 3 carbon atoms by reacting an alkane having 1 carbon atom with an alkane having 2 carbon atoms, and dehyrohalogenating the synthesized alkane to produce a fluorinated olefin such as HFC-1234yf. Patent Document 6 listed below describes a process of passing $CF_3CHFCHF_2$ (HFC-236ea) and CF_3CHFCH_2F (HFC-245eb) simultaneously through a catalyst layer and subjecting them dehydrofluorination to directly produce a mixture of HFC-1225ye (1,1,1,2,3-pentafluoropropene) and HFC-1234yf. Patent Document 7 listed below describes a process of fluorinating CX_3CXYCH_3 with HF concurrently with a dehydrofluorination reaction to produce HFC-1234yf.

Patent Document 1: WO 2007/056194

Patent Document 2: U.S. Patent Application Publication No. 2007/0179324

Patent Document 3: WO 2007/086972

Patent Document 4: WO 2007/056127

Patent Document 5: WO 2007/056128

Patent Document 6: WO 2007/117391

Patent Document 7: WO 2007/056148

Patent Document 8: WO 93/25510

Disclosure of Invention

However, these processes may often produce, in addition to HFC-1234yf as the aimed product and HFC-245eb as a precursor thereof, by-products which cannot be converted into HFC-1234yf. An object of the present invention is to provide a process capable of producing HFC-1234yf with a higher selectivity than that of the conventional methods.

The present inventors have studied about use of hexafluoropropene (HFP) as a raw material for production of HFC-1234yf, also intensively studied about appropriate procedure for carrying out hydrogenation, dehydrofluorination and distillation, and finally accomplished the present invention.

In a first aspect of the present invention, there is provided a process for producing 1,1,1,2-tetrafluoropropene (HFC-1234yf), which comprises the steps of:

a) hydrogenating a raw material of hexafluoropropene (HFP) together with 1,1,1,2,3-pentafluoropropene (HFC-1225ye) in the presence of a reducing catalyst to obtain a reaction mixture containing 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and 1,1,1,2,3-pentafluoropropane (HFC-245eb);

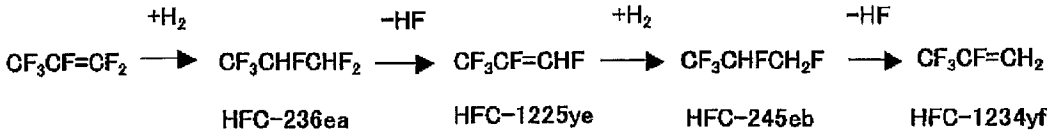
b) subjecting the reaction mixture obtained from the step a) to a dehydrofluorination reaction to obtain a reaction mixture containing 1,1,1,2,3-pentafluoropropene (HFC-1225ye) and 1,1,1,2-tetrafluoropropene (HFC-1234yf);

c) subjecting the reaction mixture obtained from the step b) to distillation to separate into a 1A fraction containing 1,1,1,2-tetrafluoropropene (HFC-1234yf) and a 2A fraction containing 1,1,1,2,3-pentafluoropropene (HFC-1225ye); and

d) using 1,1,1,2,3-pentafluoropropene (HFC-1225ye) contained in the 2A fraction for the step a),

whereby 1,1,1,2-tetrafluoropropene is obtained in the 1A fraction.

It is considered that, in the process according to the first aspect of the present invention, for producing HFC-1234yf from HFP, the following reactions successively proceed via HFC-1225ye.



The present inventors have found that the hydrogenating reaction producing HFC-236ea from HFP and the hydrogenating reaction producing HFC-245eb from HFC-1225ye can proceed under the same conditions, and also the dehydrofluorination reaction producing HFC-1225ye from HFC-236ea and the dehydrofluorination reaction producing HFC-1234yf from HFC-245eb can proceed under the same conditions.

Thus, the hydrogenations and the dehydrofluorinations are respectively carried out in the same times (in other words, by "folding" the above successive reactions), and then distillation is carried out so that HFC-1234yf is obtained. According to this process of the present invention, it becomes possible to produce HFC-1234yf with a higher selectivity.

In the process according to the above first aspect of the present invention,

the 2A fraction obtained from the step c) may contain, in addition to 1,1,1,2,3-pentafluoropropene (HFC-1225ye), at least one of 1,1,1,2,3-pentafluoropropane (HFC-245eb) and 1,1,1,2,3,3-hexafluoropropane (HFC-236ea); and

the step d) may comprise subjecting the 2A fraction to further distillation to separate into a 3A fraction containing at least one of 1,1,1,2,3-pentafluoropropane (HFC-245eb) and 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and a 4A fraction containing 1,1,1,2,3-pentafluoropropene (HFC-1225ye), subjecting the 3A fraction to the dehydrofluorination reaction of the step b) and subjecting the 4A fraction to the hydrogenating reaction of the step a).

Therefore, at least one of HFC-245eb and HFC-236ea as intermediates and HFC-1225ye can be used by returning to the each appropriate reaction stage.

However, the first aspect of the present invention is not limited thereto. For example, all of the 2A fraction as is may be subjected to the hydrogenating reaction of the step a).

In a second aspect of the present invention, there is provided a process for producing 1,1,1,2-tetrafluoropropene (HFC-1234yf), which comprises the steps of:

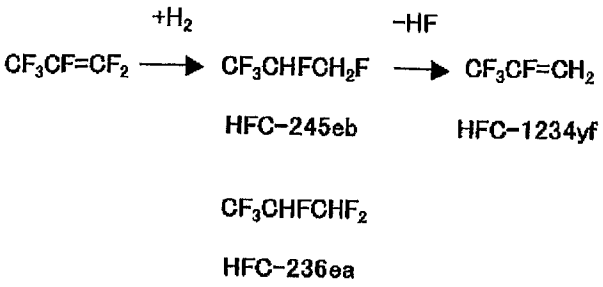
p) hydrogenating a raw material of hexafluoropropene in the presence of a reducing catalyst to obtain a reaction mixture containing 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and 1,1,1,2,3-pentafluoropropane (HFC-245eb);

q) subjecting the reaction mixture obtained from the step p) to distillation to separate into a 1B fraction containing 1,1,1,2,3-pentafluoropropane (HFC-245eb) and a 2B fraction containing 1,1,1,2,3,3-hexafluoropropane (HFC-236ea); and

r) subjecting the 1B fraction to a dehydrofluorination reaction to obtain a reaction mixture containing 1,1,1,2-tetrafluoropropene (HFC-1234yf),

whereby 1,1,1,2-tetrafluoropropene (HFC-1234yf) is obtained in the reaction mixture of the step r).

It is considered that, in the process according to the second aspect of the present invention, for producing HFC-1234yf from HFP, the following reactions proceed.



The present inventors have found that HFC-245eb is directly obtained, in addition to HFC-236ea, by hydrogenating HFP under appropriate conditions, and the resulting HFC-245eb is separated by distillation and is bydehydrofluorinated to obtain HFC-1234yf. According to this process of the present invention, it becomes possible to produce HFC-1234yf with a higher selectivity.

The process according to the above second aspect of the present invention may further comprise supplying the 2B fraction obtained from the step q) to the hydrogenating reaction of the step p).

Therefore, HFC-236ea as an intermediate can be subjected to hydrogenation to obtain HFC-245eb.

However, the second aspect of the present invention is not limited thereto. It is not required to utilize the 2B fraction for hydrogenation.

According to the present invention, 1,1,1,2-tetrafluoropropene (HFC-1234yf) can be produced with a higher selectivity by using hexafluoropropene (HFP) as a

raw material and appropriately combining hydrogenation, dehydrofluorination and distillation.

Brief Description of Drawings

Fig. 1 shows a schematic diagram for explaining a process for producing 1,1,1,2-tetrafluoropropene (HFC-1234yf) in one embodiment of the present invention.

Fig. 2 shows a schematic diagram for explaining a process for producing 1,1,1,2-tetrafluoropropene (HFC-1234yf) in another embodiment of the present invention.

Following numerals denote the following elements: 11-17, 21-25...line; R11, R21...reactor (hydrogenating reaction); R12, R22...reactor (dehydrofluorination reaction); T11, T12, T21...distillation column; F1, F2...feed (mixture); S11...first stream (reaction mixture); S12...second stream (reaction mixture); S13...third stream (1A fraction); S14...fourth stream (2A fraction); S15...fifth stream (3A fraction); S16...sixth stream (4A fraction); S21...first stream (reaction mixture); S22...second stream (1B fraction); S23...third stream (reaction mixture); and S24...fourth stream (2B fraction).

Best Mode for Carrying Out the Invention

Two embodiments of the present invention will be described in detail below with reference to the drawings.

(Embodiment 1)

The present embodiment relates to a manner in which following a hydrogenating reaction, dehydrofluorination is carried out, and then distillation is carried our ("folding" type).

Referring to Fig. 1, a raw material of hexafluoropropene (HFP) is fed from the outside to a line 11, and a sixth stream (S16) taken out of a distillation column T12 through a line 17 as mentioned below is recycled to the line 11. The sixth stream (S16) is a 4A fraction containing 1,1,1,2,3-pentafluoropropene (HFC-1225ye). Thus, the mixture of HFP and HFC-1225ye, as a feed (F1), is fed to a reactor R11 through the line 11.

The mixture of HFP and HFC-1225ye fed as the feed (F1) is subjected to hydrogenation in the presence of a reducing catalyst in the reactor R11 (in Fig. 1, supply of H_2 is omitted) to produce 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) and 1,1,1,2,3-pentafluoropropane (HFC-245eb). In the reaction mixture, although the unreacted HFP and HFC-1225ye may slightly remain, it is preferred that there is substantially no material which would not be finally converted into HFC-1234yf.

As the reducing catalyst, for example, a general reducing catalyst can be used. A preferred reducing

catalyst is a supported metal such as Pd, Pt, Rh, Ru or Re on activated carbon, a metal oxide such as alumina, or a metal fluoride. The ratio of metal supported is from 0.1 to 20% by weight, preferably from 0.1 to 10% by weight, and more preferably from 0.5 to 5% by weight.

Since ability of reduction varies depending on the kind of the catalyst and reduction may proceed excessively or may not proceed (a conversion ratio may not increase), the catalyst can be appropriately selected according to the purposes of the present embodiment.

The reaction pressure is not particularly limited and the reaction may proceed under reduced pressure, normal pressure or increased pressure, but the reaction under normal pressure or increased pressure is preferred. The pressure is preferably in a range from about 0 to 1.5 MPaG (gauge pressure), since such pressure has an advantage in that it does not require a comparatively large device for proceeding the reaction. However, it is also possible to apply a pressure out of the above range.

The reaction temperature is usually in a range from about 30 to 400°C, preferably from about 30 to 300°C, and more preferably from about 30 to 180°C. The amount of by-products can be suppressed to a comparatively small amount by the reaction temperature not being unnecessarily high. Since this reaction is an exothermic reaction, a

temperature higher than the above range may occur locally (at a part of the catalyst).

The contact time is represented by W/F0 ($g \cdot Nml^{-1} \cdot sec$) (in this case, F0 ($Nml \cdot sec^{-1}$) denotes the amount of the feed (F1) supplied to the reactor R11, and W (g) denotes the amount of the catalyst filling the reactor R11), it may be usually in a range from about 0.1 to 30, and is preferably in a range from about 0.5 to 15 (the symbol "N" in the unit means conversion into a normal condition of 0°C and 1 atm, the same shall apply hereinafter). The contact time exerts an influence on selectivity and conversion ratio, and therefore can be appropriately selected according to the purposes.

Hydrogen (H_2) used for hydrogenation is usually mixed with HFP as the raw material and HFC-1225ye in a ratio not smaller than a theoretically equivalent amount and supplied to the reactor R11. Therefore, the molar ratio in supply of H_2/(HFP and HFC-1225ye) is usually in a range from 1 to 6, and more preferably from 1 to 3.

Then, the reaction mixture obtained in the reactor R11 is taken out as a first stream (S11) through a line 12 and supplied to a reactor R12. And, HFC-236ea and HFC-245eb in the reaction mixture are subjected to dehydrofluorination to produce 1,1,1,2,3-pentafluoropropene (HFC-1225ye) and 1,1,1,2-tetrafluoropropene (HFC-1234yf). In a reaction

mixture thus obtained, unreacted HFC-236ea, HFC-245eb and so on may remain.

For the dehydrofluorination reaction, a catalyst which can be used for a general dehydrohalogenation reaction can be used. The catalyst is specifically, for example, a metal oxyfluoride or a metal fluoride, and more specifically chromium oxyfluoride, aluminum oxyfluoride, niobium fluoride, magnesium fluoride, tantalum fluoride or antimony fluoride, but is not particularly limited thereto. For another example, an activated carbon based catalyst as disclosed in Patent Document 8 listed above may also be used.

The reaction pressure is not particularly limited and the reaction may proceed under reduced pressure, normal pressure or increased pressure, but the reaction under normal pressure is preferred. The reaction under normal pressure is advantageous in comparison to the reaction under increased pressure in view of equilibrium, and has an advantage in comparison to the reaction under reduced pressure in that it does not require a comparatively large device.

The reaction temperature, in a case under normal pressure, can be in a range from about 200 to 600°C, and preferably in a range from 250 to 450°C.

The contact time is represented by W'/F0' ($g \cdot Nml^{-}$

^{1}·sec) (in this case, F0' (Nml·sec^{-1}) denotes the amount of the first stream (S11) and, if any, a below-mentioned fifth stream (S15) supplied to the reactor R12, and W' (g) denotes the amount of the catalyst filling the reactor R12) may be usually in a range from about 0.1 to 120, and is preferably in a range from about 0.5 to 60.

In the reactions of the present embodiment, the dehydrofluorination reaction is a rate-limiting step.

Then, the reaction mixture obtained in the reactor R12 after dehydrofluorination, is taken out as a second stream (S12) through a line 13 and supplied to a distillation column T11. The second stream (S12) contains HFC-1234yf (normal boiling point of about -29°C) and HFC-1225ye (normal boiling points of about -19.5°C (Z-isomer) and about -15.3°C (E-isomer)) and is separated by distillation into a 1A fraction containing HFC-1234yf (low-boiling component) and a 2A fraction containing HFC-1225ye (high-boiling component).

The 1A fraction is taken out of the distillation column T11 as a third stream (S13) through a line 14 . The 1A fraction is preferably composed of HFC-1234yf substantially, and by the 1A fraction, HFC-1234yf can be obtained.

The 2A fraction is taken out of the distillation column T11 as a fourth stream (S14) through a line 15. The

2A fraction may generally contain, in addition to HFC-1225ye, HFC-245eb (normal boiling point of about 23°C) and/or HFC-236ea (normal boiling point of about 6°C).

The 2A fraction thus obtained after taking out of the distillation column T11 as the fourth stream (S14), is supplied to a further distillation column T12 and separated by distillation into a 3A fraction containing at least one of, generally both of, HFC-245eb and HFC-236ea (high-boiling components) and a 4A fraction containing HFC-1225ye (low-boiling component). The 3A fraction is taken out of the distillation column T12 through a line 16 as a fifth stream (S15), and may be returned to the reactor R12, where it is subjected to the dehydrofluorination reaction. The 4A fraction is taken out of the distillation column T12 through a line 17 as the sixth stream (S16), and supplied to the reactor R11 together with HFP as the feed (F1) as mentioned above, where it is subjected to the hydrogenating reaction.

As described above, according to the present embodiment, HFC-1234yf can be produced with a high selectivity by carrying out the successive reactions for obtaining HFC-1234yf from HFP through HFC-1225ye in the simplified process. The process of the present embodiment can be conducted continuously.

Although an amount of impurities produced in the

present embodiment is quite small, low-boiling and high-boiling impurities may be removed from the stream(s) (e.g. the product stream and the recycling stream) by distillation, if appropriate. Hydrogen fluoride (HF) produced during the step may be separated and removed by washing with water and/or distillation, if appropriate. Although the unreacted hydrogen (H_2) may exist in the stream(s), it may be appropriately treated by, for example, separation and removal, or recycling to the reactor R11.

(Embodiment 2)

The present embodiment relates to a manner in which following a hydrogenating reaction, distillation is carried out, and then dehydrofluorination is carried out ("direct" type). Hereinafter, the present embodiment is similar to Embodiment 1 unless otherwise specified.

Referring to Fig. 2, a raw material of hexafluoropropene (HFP) is fed from the outside to a line 21 and a fourth stream (S24) taken out of a distillation column T21 through a line 24 as mentioned below is recycled to the line 21. The fourth stream (S24) is a 2B fraction containing HFC-236ea. Thus, the mixture of HFP and HFC-236ea, as a feed (F2), is fed to a reactor R21 through the line 21. However, it should be noted that feed of HFC-236ea is not essential to the present embodiment.

The mixture of HFP and HFC-236ea fed as the feed (F2) is subjected to hydrogenation in the presence of a reducing catalyst in the reactor R21 (in Fig. 2, supply of H_2 is omitted) to produce HFC-236ea and HFC-245eb. In the present embodiment, even if only HFP is fed as the feed (F2), HFC-245eb can be produced directly from HFP. In the reaction mixture, HFC-1225ye may also be contained.

As the reducing catalyst, any appropriate reducing catalyst capable of directly producing HFC-245eb from HFP, for example, those mentioned in Embodiment 1 may be used accordingly.

Since ability of reduction varies depending on the kind of the catalyst and reduction may proceed excessively or may not proceed (a conversion ratio may not increase), the catalyst can be appropriately selected according to the purposes of the present embodiment.

The reaction pressure is not particularly limited and the reaction may proceed under reduced pressure, normal pressure or increased pressure, but the reaction under normal pressure or increased pressure is preferred. The pressure is preferably in a range from about 0 to 1.5 MPaG (gauge pressure), since such pressure has an advantage in that it does not require a comparatively large device for proceeding the reaction. However, it is also possible to apply a pressure out of the above range.

The reaction temperature is usually in a range from about 30 to 500°C, preferably from about 30 to 400°C, and more preferably from about 30 to 300°C. The amount of by-products can be suppressed to a comparatively small amount by the reaction temperature not being unnecessarily high. Since this reaction is an exothermic reaction, a temperature higher than the above range may occur locally (at a part of the catalyst).

The contact time is represented by W/F0 ($g \cdot Nml^{-1} \cdot sec$) (in this case, F0 ($Nml \cdot sec^{-1}$) denotes the amount of the feed (F2) supplied to the reactor R21, and W (g) denotes the amount of the catalyst filling the reactor R21), it may be usually in a range from about 0.1 to 30, and is preferably in a range from about 0.5 to 15. The contact time exerts an influence on selectivity and conversion ratio, and therefore can be appropriately selected according to the purposes.

Hydrogen (H_2) used for hydrogenation is usually mixed with HFP as the raw material (and HFC-236ea when it exists in the feed as in the present embodiment) in a ratio not smaller than a theoretically equivalent amount and supplied to the reactor R21. Therefore, the molar ratio in supply (which corresponds to the volume ratio in a gaseous state) of H_2/HFP (or H_2/(HFP and HFC-236ea) when HFC-236ea exists in the feed as in the present embodiment) is usually in a

range from 1 to 6, and more preferably from 1 to 4.

Then, the reaction mixture obtained in the reactor R21 is taken out as a first stream (S21) through a line 22 and supplied to a distillation column T21. The first stream (S21) contains HFC-245eb and HFC-236ea and is separated by distillation into a 1B fraction containing HFC-245eb (high-boiling component) and a 2B fraction containing HFC-236ea (low-boiling component).

The 1B fraction is taken out of the distillation column T21 through a line 23 as a second stream (S22) and supplied to a reactor R22. And, HFC-245eb in the 1B fraction is subjected to dehydrofluorination to produce HFC-1234yf.

The conditions of the dehydrofluorination reaction are the same as those of Embodiment 1.

The reaction pressure is not particularly limited and the reaction may proceed under reduced pressure, normal pressure or increased pressure, but the reaction under normal pressure is preferred. The reaction under normal pressure is advantageous in comparison to the reaction under increased pressure in view of equilibrium, and has an advantage in comparison to the reaction under reduced pressure in that it does not require a comparatively large device.

The reaction temperature, in a case under normal

pressure, can be in a range from about 200 to 600°C, and preferably in a range from 250 to 450°C.

The contact time is represented by W'/F0' ($g \cdot Nml^{-1} \cdot sec$) (in this case, F0' ($Nml \cdot sec^{-1}$) denotes the amount of the second stream (S22) and, if any, the below-mentioned recycling stream supplied to a reactor R22, and W' (g) denotes the amount of the catalyst filling the reactor R22), it may be usually in a range from about 0.1 to 120, and is preferably in a range from about 0.5 to 60.

Although the unreacted HFC-245eb may also remain, the reaction mixture thus obtained preferably contains HFC-1234yf in high purity. Therefore, HFC-1234yf can be obtained. If desired, the reaction mixture may be separated into a fraction containing HFC-1234yf and a fraction containing HFC-245eb, and the latter fraction may be returned (recycling stream) to the reactor R22, where it is subjected to the dehydrofluorination reaction. Also in the reactions of the present embodiment, the dehydrofluorination reaction is a rate-limiting step.

On the other hand, the 2B fraction is taken out of the distillation column T21 through a line 24 as the fourth stream (S24), and supplied to the reactor R21 together with HFP as the feed (F2) as mentioned above, where it is subjected to the hydrogenating reaction. The 2B fraction may generally contain HFC-1225ye, in addition to HFC-236ea.

As described above, according to the present embodiment, HFC-1234yf can be produced with a high selectivity by the very simple process which utilizes the reaction capable of directly obtaining HFC-245eb from HFP. The process of the present embodiment can also be conducted continuously.

Although an amount of impurities produced in the present embodiment is quite small, low boiling and high boiling impurities may be removed from the stream(s) (e.g. the product stream and the recycling stream) by distillation, if appropriate. Hydrogen fluoride (HF) produced during the step may be separated and removed by washing with water and/or distillation, if appropriate. Although the unreacted hydrogen (H_2) may exist in the stream(s), it may be appropriately treated by, for example, separation and removal, or recycling to the reactor R21.

[Example 1]

The process of the present invention was carried out in accordance with Embodiment 1 described in detail with reference to Fig. 1.

As a raw material, HFP was used in a gaseous state. This raw material and a sixth stream (S16) recycled from the distillation column T12 were combined and then fed, as a feed (F1), to the reactor R11, where the feed was

subjected to the hydrogenation reaction in the presence of a reducing catalyst. As the reducing catalyst, an activated carbon-supported Pd catalyst (ratio of Pd supported: 3% by weight) was used. The reaction conditions were as follows: The reaction temperature was 200°C, and the reaction pressure was normal pressure. The volume ratio in supply of H_2/(HFP and HFC-1225ye) was adjusted to 3. W/F0 = 8 ($g \cdot Nml^{-1} \cdot sec$), wherein F0 ($Nml \cdot sec^{-1}$) denotes the amount of the feed (F1) supplied to the reactor R11, and W (g) denotes the amount of the catalyst filling the reactor R11.

The reaction mixture obtained in the reactor R11 was taken out as a first stream (S11) and supplied to the reactor R12, where it was subjected to the dehydrofluorination reaction. A fifth stream (S15) recycled from the distillation column T12 was also supplied to the reactor R12, and subjected to the dehydrofluorination reaction. As the catalyst, a chromium oxyfluoride catalyst (fluorine content: about 31.4% by weight) was used. The reaction conditions were as follows: The reaction temperature was 400°C, and the reaction pressure was normal pressure. W'/F0' = 20 ($g \cdot Nml^{-1} \cdot sec$), wherein F0' ($Nml \cdot sec^{-1}$) denotes the amount of the first stream (S11) and the fifth stream (S15) supplied to the reactor R12, and W' (g) denotes the amount of the catalyst

filling the reactor R12.

The reaction mixture obtained in the reactor R12 after the dehydrofluorination was taken out as a second stream (S12) and transferred to the distillation column T11, where it was separated into a third stream (S13) as a low-boiling part and a fourth stream (S14) as a high-boiling part. The resultant fourth stream (S14) was transferred to the distillation column T12, where it was separated into a fifth stream (S15) as a high-boiling part and a sixth stream (S16) as a low-boiling part. The resultant fifth stream (S15) and sixth stream (S16) were recycled entirely to the reactor R12 and the reactor R11 respectively, as described above.

Twelve hours after starting the operation, compositions of the feed (F1) and the first to sixth streams (S11 to S16) were analyzed by gas chromatography to determine the flow rate of each component excluding hydrogen (H_2) and hydrogen fluoride (HF). The results are shown in Table 1. In the table, the symbol "-" means no detection, and "trace" means existence only in a trace amount.

Table 1

	Flow rate (kmol/hr)						
	F1	S11	S12	S13	S14	S15	S16
HFP	0.51	-	-	-	-	-	-
HFC-236ea	-	0.51	0.08	-	0.08	0.08	-
HFC-245eb	-	0.49	0.05	-	0.05	0.05	-
HFC-1234yf	-	-	0.50	0.50	-	-	-
HFC-1225ye	0.49	-	0.49	-	0.49	-	0.49
Impurities	trace	trace	0.02	0.01	0.01	0.01	trace

It is confirmed from Table 1 that HFC-1234yf can be obtained as the third stream (S13), which corresponds to the 1A fraction, with a high yield.

[Example 2]

The process of the present invention was carried out in accordance with Embodiment 2 described in detail with reference to Fig. 2.

As a raw material, HFP was used in a gaseous state. This raw material and a fourth stream (S24) recycled from the distillation column T21 were combined and then fed, as a feed (F2), to the reactor R21, where the feed was subjected to the hydrogenation reaction in the presence of a reducing catalyst. As the reducing catalyst, an activated carbon-supported Pd catalyst (ratio of Pd supported: 3% by weight) was used. The reaction conditions were as follows: The reaction temperature was 200°C, and the reaction pressure was normal pressure. The volume

ratio in supply of H_2/(HFP and HFC-236ea) was adjusted to 4. W/F0 = 8 ($g \cdot Nml^{-1} \cdot sec$), wherein F0 ($Nml \cdot sec^{-1}$) denotes the amount of the feed (F2) supplied to the reactor R21, and W (g) denotes the amount of the catalyst filling the reactor R21.

The reaction mixture obtained in the reactor R21 was taken out as a first stream (S21) and supplied to the distillation column T21, where it was separated into a second stream (S22) as a high-boiling part and a fourth stream (S24) as a low-boiling part.

The resulting second stream (S22) was supplied to the reactor R22, where it was subjected to the dehydrofluorination reaction. As the catalyst, a chromium oxyfluoride catalyst (fluorine content: about 31.4% by weight) was used. The reaction conditions were as follows: The reaction temperature was 400°C, and the reaction pressure was normal pressure. W'/F0' = 20 ($g \cdot Nml^{-1} \cdot sec$), wherein F0' ($Nml \cdot sec^{-1}$) denotes the amount of the second stream (S22) supplied to the reactor R22, and W' (g) denotes the amount of the catalyst filling the reactor R22.

On the other hand, the fourth stream (S24) was recycled entirely to the reactor 21, as described above.

Twelve hours after starting the operation, compositions of the feed (F2) and the first to fourth streams (S21 to S24) were analyzed by gas chromatography to

determine the flow rate of each component excluding hydrogen (H_2) and hydrogen fluoride (HF). The results are shown in Table 2. In the table, the symbol "-" means no detection, and "trace" means existence only in a trace amount.

Table 2

	Flow rate (kmol/hr)				
	F2	S21	S22	S23	S24
HFP	0.2	-	-	-	-
HFC-1225ye	trace	trace	-	-	trace
HFC-236ea	0.9	0.9	-	-	0.9
HFC-245eb	-	0.2	0.2	0.016	-
HFC-1234yf	-	-	-	0.18	-
Impurities	trace	trace	trace	0.004	trace

It is confirmed from Table 2 that HFC-1234yf can be obtained in the third stream (S23), which corresponds to the reaction mixture after dehydrofluorination, in a yield of 90%. Since HFC-245eb in the third stream is an intermediate, a high yield of 97% or more can be expected when HFC-245eb is separated and recycled to the dehydrofluorinated reaction to obtain HFC-1234yf.

Industrial Applicability

1,1,1,2-tetrafluoropropene (HFC-1234yf) can be used as a refrigerant substance, and a process for producing HFC-1234yf using hexafluoropropene (HFP) as a raw material can

be expected to be useful as a process for producing a substitute refrigerant.

The present application claims a priority to United States Provisional Application No. 61/017,052 filed on December 27, 2007, entitled "PROCESS FOR PRODUCING 1,1,1,2-TETRAFLUOROPROPENE". The contents of that application are incorporated herein by the reference thereto in their entirety.

CLAIMS

1. A process for producing 1,1,1,2-tetrafluoropropene, which comprises the steps of:

a) hydrogenating a raw material of hexafluoropropene together with 1,1,1,2,3-pentafluoropropene in the presence of a reducing catalyst to obtain a reaction mixture containing 1,1,1,2,3,3-hexafluoropropane and 1,1,1,2,3-pentafluoropropane;

b) subjecting the reaction mixture obtained from the step a) to a dehydrofluorination reaction to obtain a reaction mixture containing 1,1,1,2,3-pentafluoropropene and 1,1,1,2-tetrafluoropropene;

c) subjecting the reaction mixture obtained from the step b) to distillation to separate into a 1A fraction containing 1,1,1,2-tetrafluoropropene and a 2A fraction containing 1,1,1,2,3-pentafluoropropene; and

d) using 1,1,1,2,3-pentafluoropropene contained in the 2A fraction for the step a),

whereby 1,1,1,2-tetrafluoropropene is obtained in the 1A fraction.

2. The process according to claim 1, wherein the 2A faction obtained from the step c) contains, in addition to 1,1,1,2,3-pentafluoropropene, at least one of 1,1,1,2,3-

pentafluoropropane and 1,1,1,2,3,3-hexafluoropropane; and

the step d) comprises subjecting the 2A fraction to further distillation to separate into a 3A fraction containing at least one of 1,1,1,2,3-pentafluoropropane and 1,1,1,2,3,3-hexafluoropropane and a 4A fraction containing 1,1,1,2,3-pentafluoropropene, subjecting the 3A fraction to the dehydrofluorination reaction of the step b), and subjecting the 4A fraction to the hydrogenating reaction of the step a).

3. A process for producing 1,1,1,2-tetrafluoropropene, which comprises the steps of:

p) hydrogenating a raw material of hexafluoropropene in the presence of a reducing catalyst to obtain a reaction mixture containing 1,1,1,2,3,3-hexafluoropropane and 1,1,1,2,3-pentafluoropropane;

q) subjecting the reaction mixture obtained from the step p) to distilling to separate into a 1B fraction containing 1,1,1,2,3-pentafluoropropane and a 2B fraction containing 1,1,1,2,3,3-hexafluoropropane; and

r) subjecting the 1B fraction to a dehydrofluorination reaction to obtain a reaction mixture containing 1,1,1,2-tetrafluoropropene,

whereby 1,1,1,2-tetrafluoropropene is obtained in the reaction mixture of the step r).

4. The process according to claim 3, which further comprises supplying the 2B fraction obtained from the step q) to the hydrogenating reaction of the step p).

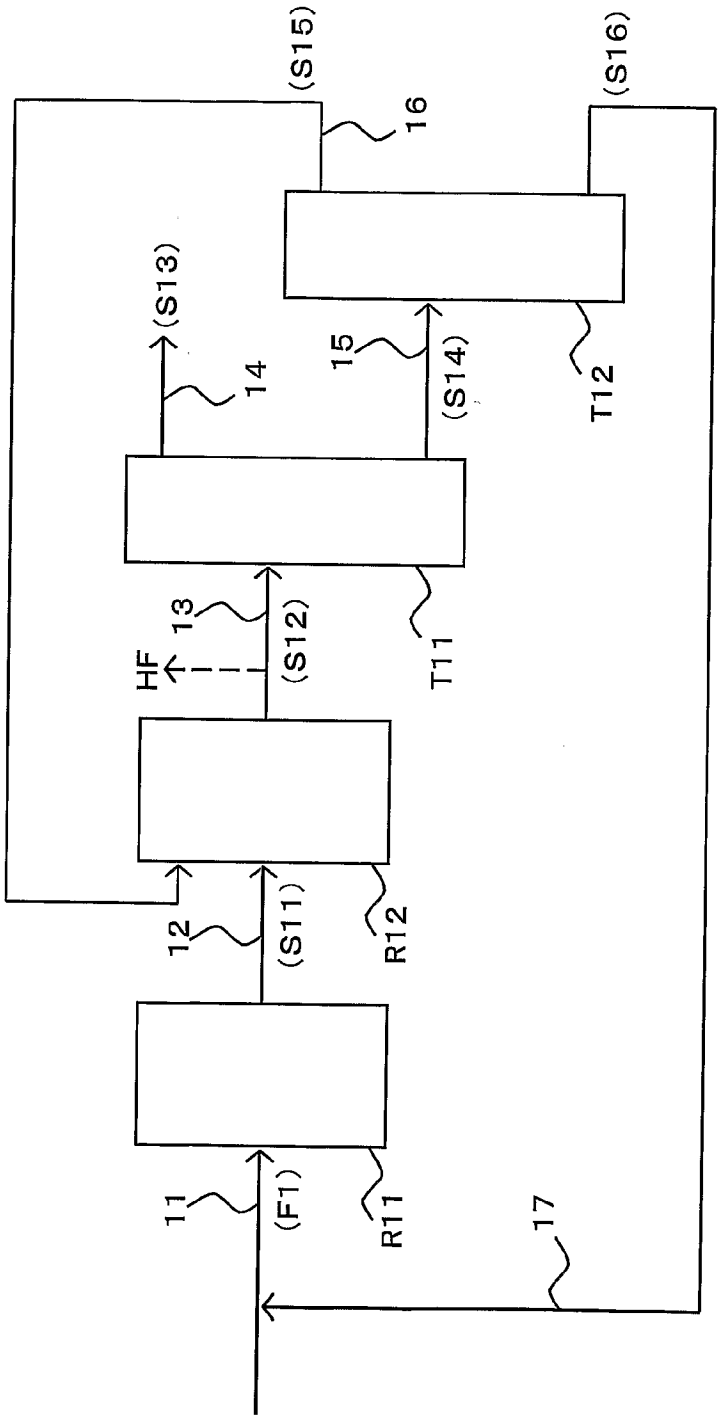


Fig. 1

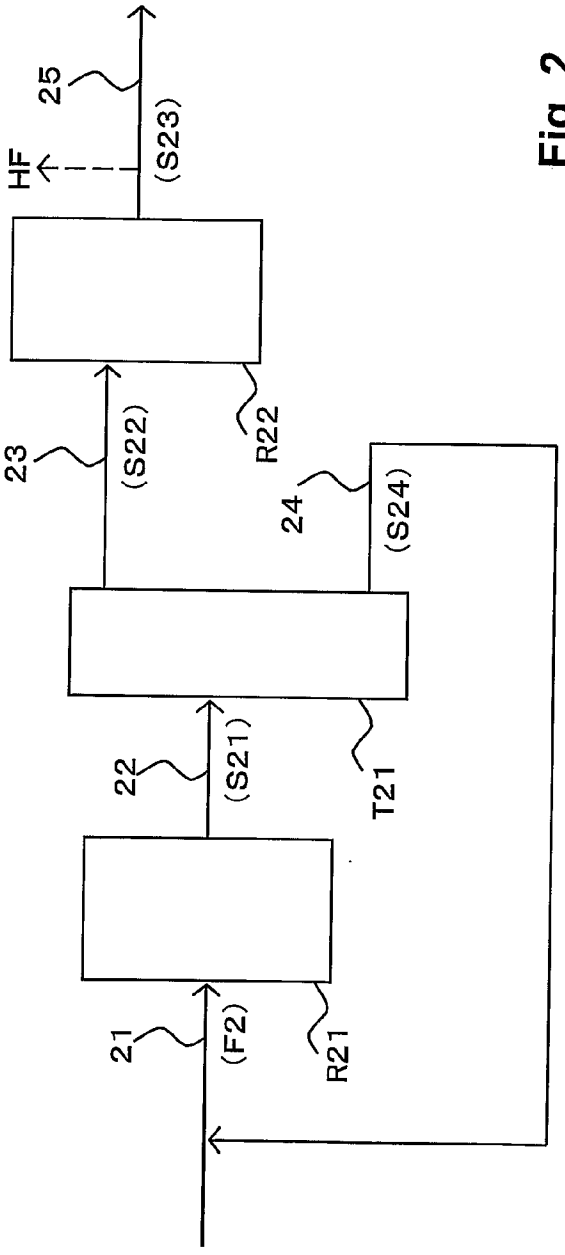


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2008/073902

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C17/25 C07C17/354 C07C17/383 C07C19/08 C07C21/18

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 practical, 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.
A	US 2007/179324 A1 (VAN DER PUY MICHAEL [US] ET AL) 2 August 2007 (2007-08-02) cited in the application abstract examples 1-8	1,3
A	US 4 086 407 A (FOZZARD GEORGE B) 25 April 1978 (1978-04-25) abstract examples 1,3	1,3

☐ 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 document but published on or after the international filing date

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 March 2009	11/03/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Delanghe, Patrick

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2008/073902

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007179324 A1	02-08-2007	WO 2008057794 A1	15-05-2008
US 4086407 A	25-04-1978	US 3996299 A	07-12-1976
		US B330736 I5	03-02-1976

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(71) **Applicant** *(for all designated States except US)*: **INEOS FLUOR HOLDINGS LIIMITED** [GB/GB]; P O Box 13, The Heath, Tuncorn, Cheshire WA7 4QF (GB).

(72) **Inventors; and**

(75) **Inventors/Applicants** *(for US only)*: **SMITH, John, William** [GB/GB]; Ineos Fluor Holdings Liimited, P O Box 13, The Heath, Tuncorn, Cheshire WA7 4QF (GB). **MCGUINESS, Claire** [GB/GB]; Ineos Fluor Holdings Liimited, P O Box 13, The Heath, Tuncorn, Cheshire WA7 4QF (GB). **SHARRATT, Andrew, Paul** [GB/GB]; Ineos Fluor Holdings Liimited, P O Box 13, The Heath, Tuncorn, Cheshire WA7 4QF (GB).

(74) **Agent**: **BAKER, Colin**; POTTER CLARKSON LLP, Park View House, 58 The Ropewalk, Nottingham NG1 5DD (GB).

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(54) **Title**: PROCESS

(57) **Abstract**: The invention provides a process for the preparation of 2,3,3,3-tetrafluoropropene (1234yf) comprising (a) contacting 1,1,1-trifluoro-2,3-difluoropropane (243db) with hydrogen fluoride (HF) in the presence of a zinc/chromia catalyst to produce a compound having the formula CF_3CHFCH_2X, wherein X is Cl or F, and (b) dehydrohalogenating the compound of formula CF_3CHFCH_2X to produce 1234yf.

Process

The invention relates to a process for preparing 2,3,3,3-tetrafluoropropene. In particular, the invention relates to a process for preparing 2,3,3,3-tetrafluoropropene comprising fluorinating 1,1,1-trifluoro-2,3-dichloropropane and dehydrohalogenating a compound formed from the fluorination to produce 2,3,3,3-tetrafluoropropene.

2,3,3,3-tetrafluoropropene is also known as HFO-1234yf, HFC-1234yf or simply 1234yf. Hereinafter, unless otherwise stated, 2,3,3,3-tetrafluoropropene will be referred to as 1234yf. The known processes for preparing 1234yf typically suffer from disadvantages such as low yields, and/or the handling of toxic and/or expensive reagents, and/or the use of extreme conditions, and/or the production of toxic by-products. Methods for the preparation of 1234yf have been described in, for example, Journal Fluorine Chemistry (82), 1997, 171-174. In this paper, 1234yf is prepared by the reaction of sulphur tetrafluoride with trifluoroacetylacetone. However, this method is only of academic interest because of the hazards involved in handling the reagents and their expense. Another method for the preparation of 1234yf is described in US-2931840. In this case, pyrolysis of C1 chlorofluorocarbons with or without tetrafluoroethylene was purported to yield 1234yf. However, the yields described were very low and again it was necessary to handle hazardous chemicals under extreme conditions. It would also be expected that such a process would produce a variety of very toxic by-products. In addition to addressing the disadvantages of the known methods, it would be desirable to provide a new method for the preparation of 1234yf that use only readily available feedstocks.

The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

The present invention addresses the foregoing deficiencies of the known routes for preparing 1234yf by providing a process for its preparation comprising (a) contacting 1,1,1-trifluoro-2,3-dichloropropane with hydrogen fluoride (HF) in the presence of a zinc/chromia catalyst to produce a compound having the formula CF_3CHFCH_2X, wherein X is Cl or F; and (b) dehydrohalogenating the compound of formula CF_3CHFCH_2X to produce 1234yf.

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1,1,1-trifluoro-2,3-dichloropropane is also known as HCFC-243db or simply 243db. Hereinafter, unless otherwise stated, 1,1,1-trifluoro-2,3-dichloropropane will be referred to as 243db. For the avoidance of doubt, a compound of formula CF_3CHFCH_2X (wherein X = Cl or F) may be either 1,1,1,2,3-pentafluoropropane (X = F, also known as HFC 245eb or just 245eb) or 1,1,1,2-tetrafluoro-3-chloropropane (X = Cl, also known as HFC 244eb or just 244eb), or a combination thereof.

Unless otherwise stated, as used herein, by the term "dehydrohalogenation" (or dehydrohalogenating), we refer to the removal of hydrogen chloride (HCl) or hydrogen fluoride (HF) from the compound of formula CF_3CHFCH_2X. Thus the term "dehydrohalogenation" includes "dehydrofluorination" and "dehydrochlorination" of the compound of formula CF_3CHFCH_2X.

Step (a) of the process of the invention comprises contacting 243db with HF in the presence of a zinc/chromia catalyst to produce a compound having the formula CF_3CHFCH_2X, i.e. step (a) is a fluorination step. The fluorination may be carried out in the vapour and/or liquid phase and at a temperature of from about -70 to about 400 °C. The process may be carried out at atmospheric, sub- or super-atmospheric pressure, preferably from about 0 to about 30 bara.

The catalyst in step (a) may be used in an amount of from about 0.01 to about 50 % by weight, such as from about 0.1 to about 30%, for example from about 0.5 to about 20%, based on the combined weight of 243db and HF.

Step (b) of the process of the invention may be carried out by any suitable reactions conditions effective to dehydrohalogenate (i.e. dehydrochlorinate or dehydrofluorinate) the compound of formula CF_3CHFCH_2X to produce 1234yf. Preferably, the dehydrohalogenation is carried out in the vapour and/or liquid phase and may be carried out at a temperature of from about -70 to about 1000 °C (e.g. about 0 to about 400 °C). The process may be carried out at atmospheric sub- or super atmospheric pressure, preferably from about 0 to about 30 bara.

The dehydrohalogenation may be induced thermally, may be base-mediated and/or may be catalysed by any suitable catalyst. Suitable catalysts include metal and carbon based catalysts such as those comprising activated carbon, main group (e.g. alumina-based

catalysts) and transition metals, such as chromia-based catalysts (e.g. zinc/chromia) or nickel-based catalysts (e.g. nickel mesh).

One preferred method of effecting the dehydrohalogenation of the compound of formula CF_3CHFCH_2X to produce 1234yf is by contacting CF_3CHFCH_2X with a metal catalyst, such as a chromia-based (e.g. zinc/chromia) catalyst. Thus, steps (a) and (b) may be carried out in a "one-pot" manner, i.e. simultaneously. Alternatively, when both steps (a) and (b) are carried out in the presence of a metal catalyst, such as a chromia-based (e.g. zinc/chromia) catalyst, the fluorination and dehydrohalogenation reactions may be carried out in two discrete steps, for example using two or more discrete reaction zones or vessels.

Step (a) and/or step (b) can be carried out in any suitable apparatus, such as a static mixer, a stirred tank reactor or a stirred vapour-liquid disengagement vessel. Preferably, this or any other apparatus described herein is made from one or more materials that are resistant to corrosion, e.g. Hastelloy® or Inconel®. The process may be carried out batch-wise or continuously.

When both steps (a) and (b) are carried out in the presence of a zinc/chromia catalyst, the reaction conditions for each step (a) and (b) may be the same (e.g. in a one-pot process) or different. Preferably, the reaction conditions when steps (a) and (b) are carried out in the presence of a zinc/chromia catalyst can be selected to be different so as to optimise the fluorination and dehydrohalogenation reactions, respectively. This is explained in more detail below.

Fluorination step (a) preferably is conducted at a temperature of from about 0 to about 390 °C, such as from about 100 to about 380 °C or from about 200 to about 370 °C (e.g. from about 240 to about 260 °C). When conducted in the presence of a zinc/chromia catalyst, step (b) preferably is conducted at a temperature of from about 200 to about 360 °C, such as from about 240 to about 340 °C.

It is currently considered to be advantageous to use a higher pressure in step (a) (to promote fluorination) than in step (b) (to promote dehydrohalogenation). Thus, step (a) preferably is carried out from about 5 to about 28 bara, such as from about 10 to about 25 bara (e.g. 15 to 20 bara), whereas step (b) preferably is carried out from about 0.01 to

about 25 bara or about 0.1 to about 20 bara, such as from about 1 to about 10 bara (e.g. 1 to 5 bara).

Fluorination step (a) of the invention is carried out by contacting 243db with HF. Step (b) of the invention may be carried out in the presence of HF. For example residual HF from step (a) may be present, and/or HF from a separate feed. Alternatively, step (b) may be carried out in the absence of HF, for example following separation of the compound of formula CF_3CHFCH_2X from HF prior to step (b), and with no additional co-feed of HF. In certain embodiments it may be desirable to use some HF in order to prevent and/or retard excessive decomposition of the organic feed and/or coking of the catalyst in step (b).

When both steps (a) and (b) are carried out in the presence of a zinc/chromia catalyst and HF, the molar ratio of HF:organics can be selected to be different in each step so as to promote fluorination in step (a) and dehydrohalogenation in step (b). For example, the molar ratio of HF:organics (e.g. 243db) in step (a) preferably is from about 1:1 to about 100:1, such as from about 2:1 to about 50:1, for example from about 5:1 to about 40:1 (e.g. from about 10:1 to about 30:1). For step (b), the molar ratio of HF:organics (e.g. the compound of formula CF_3CHFCH_2X) preferably is from about 0.01:1 to about 50:1, such as from about 0.1:1 to about 40:1, for example from about 0.5:1 to about 30:1 or about 2:1 to about 15:1 (e.g. from about 10:1 to about 20:1 or from about 5:1 to about 10:1).

Another way of increasing the concentration of HF in step (a) relative to step (b) (thereby facilitating the fluorination/dehydrohalogenation reactions in these steps) is by adding a diluent gas (e.g. nitrogen) to step (b).

Another preferred method of effecting the dehydrohalogenation of the compound of formula CF_3CHFCH_2X to produce 1234yf is by contacting CF_3CHFCH_2X with a base (base-mediated dehydrohalogenation).

This base-mediated dehydrohalogenation process of step (b) comprises contacting the CF_3CHFCH_2X with base such as a metal hydroxide or amide (preferably a basic metal hydroxide or amide, e.g. an alkali or alkaline earth metal hydroxide or amide).

Unless otherwise stated, as used herein, by the term "alkali metal hydroxide", we refer to a compound or mixture of compounds selected from lithium hydroxide, sodium

hydroxide, potassium hydroxide, rubidium hydroxide and caesium hydroxide. Similarly, by the term "alkali metal amide", we refer to a compound or mixture of compounds selected from lithium amide, sodium amide, potassium amide, rubidium amide and caesium amide.

Unless otherwise stated, as used herein, by the term "alkaline earth metal hydroxide", we refer to a compound or mixture of compounds selected from beryllium hydroxide, magnesium hydroxide, calcium hydroxide, strontium hydroxide and barium hydroxide. Similarly, by the term "alkaline earth metal amide", we refer to a compound or mixture of compounds selected from beryllium amide, magnesium amide, calcium amide, strontium amide and barium amide.

Typically, the base-mediated dehydrohalogenation process of step (b) is conducted at a temperature of from -50 to 300 °C. Preferably, the process is conducted at a temperature of from 20 to 250 °C, for example from 50 to 200 °C. The base-mediated dehydrohalogenation may be conducted at a pressure of from 0 to 30 bara.

The reaction time for the base-mediated dehydrohalogenation process of step (b) may vary over a wide range. However, the reaction time will typically be in the region of from 0.01 to 100 hours, such as from 0.1 to 50 hours, e.g. from 1 to 20 hours.

Of course, the skilled person will appreciate that the preferred conditions (e.g. temperature, pressure and reaction time) for conducting the base-mediated dehydrohalogenation may vary depending on a number of factors such as the nature of the compound of formula CF_3CHFCH_2X, the base being employed, and/or the presence of a catalyst etc.

The base-mediated dehydrohalogenation process of step (b) may be carried out in the presence or absence of a solvent. If no solvent is used, the compound of formula CF_3CHFCH_2X may be passed into or over molten base or hot base, for example in a tubular reactor. If a solvent is used, in some embodiments a preferred solvent is water, although many other solvents may be used. In some embodiments solvents such as alcohols (e.g. propan-1-ol), diols (e.g. ethylene glycol) and polyols such as polyethylene glycol (e.g. PEG200 or PEG300) may be preferred. These solvents can be used alone or in combination. In further embodiments, solvents from the class known as polar aprotic solvents may be preferred. Examples of such polar aprotic solvents include

diglyme, sulfolane, dimethylformamide (DMF), dioxane, acetonitrile, hexamethylphosphoramide (HMPA), dimethyl sulphoxide (DMSO) and N-methyl pyrrolidone (NMP). The boiling point of the solvent is preferably such that it does not generate excessive pressure under reaction conditions.

A preferred base is an alkali metal hydroxide selected from the group consisting of lithium hydroxide, sodium hydroxide and potassium hydroxide, more preferably, sodium hydroxide and potassium hydroxide and most preferably potassium hydroxide.

Another preferred base is an alkaline earth metal hydroxide selected from the group consisting of magnesium hydroxide and calcium hydroxide, more preferably calcium hydroxide.

The base is typically present in an amount of from 1 to 50 weight % based on the total weight of the components which make up step (b). Preferably, the base is present in an amount of from 5 to 30 weight %.

The molar ratio of base to compound of formula CF_3CHFCH_2X is typically from 1:20 to 50:1, preferably from 1:5 to 20:1, for example from 1:2 to 10:1.

As mentioned above, the base-mediated dehydrohalogenation may preferably employ water as the solvent. Thus, the dehydrohalogenation reaction may preferably use an aqueous solution of at least one base, such as an alkali (or alkaline earth) metal hydroxide, without the need for a co-solvent or diluent. However, a co-solvent or diluent can be used for example to modify the system viscosity, to act as a preferred phase for reaction by-products, or to increase thermal mass. Useful co-solvents or diluents include those that are not reactive with or negatively impact the equilibrium or kinetics of the process and include alcohols such as methanol and ethanol; diols such as ethylene glycol; ethers such as diethyl ether, dibutyl ether; esters such as methyl acetate, ethyl acetate and the like; linear, branched and cyclic alkanes such as cyclohexane, methylcyclohexane; fluorinated diluents such as hexafluoroisopropanol, perfluorotetrahydrofuran and perfluorodecalin.

The base-mediated dehydrohalogenation of step (b) is preferably conducted in the presence of a catalyst. The catalyst is preferably a phase transfer catalyst which facilitates the transfer of ionic compounds into an organic phase from, for example, a

water phase. If water is used as a solvent, an aqueous or inorganic phase is present as a consequence of the alkali metal hydroxide and an organic phase is present as a result of the fluorocarbon. The phase transfer catalyst facilitates the reaction of these dissimilar components. While various phase transfer catalysts may function in different ways, their mechanism of action is not determinative of their utility in the present invention provided that they facilitate the dehydrohalogenation reaction. The phase transfer catalyst can be ionic or neutral and is typically selected from the group consisting of crown ethers, onium salts, cryptands and polyalkylene glycols and derivatives thereof (e.g. fluorinated derivatives thereof).

An effective amount of the phase transfer catalyst should be used in order to effect the desired reaction, influence selectivity to the desired products or enhance the yield; such an amount can be determined by limited experimentation once the reactants, process conditions and phase transfer catalyst are selected. Typically, the amount of catalyst used relative to the amount of compound of formula CF_3CHFCH_2X present is from 0.001 to 20 mol %, such as from 0.01 to 10 mol %, e.g. from 0.05 to 5 mol %.

Crown ethers are cyclic molecules in which ether groups are connected by dimethylene linkages. Crown ethers form a molecular structure that is believed to be capable of receiving or holding the alkali metal ion of the hydroxide and to thereby facilitate the reaction. Particularly useful crown ethers include 18-crown-6 (especially in combination with potassium hydroxide), 15-crown-5 (especially in combination with sodium hydroxide) and 12-crown-4 (especially in combination with lithium hydroxide).

Derivatives of the above crown ethers are also useful, such as dibenzyl-18-crown-6, dicyclohexanyl-18-crown-6, dibenzyl-24-crown-8 and dibenzyl-12-crown-4. Other compounds analogous to the crown ethers and useful for the same purpose are compounds which differ by the replacement of one or more of the oxygen atoms by other kinds of donor atoms, particularly N or S. Fluorinated derivatives of all the above may also be used.

Cryptands are another class of compounds useful in the base-mediated dehydrohalogenation as phase transfer catalysts. These are three dimensional polymacrocyclic chelating agents that are formed by joining bridgehead structures with chains that contain properly spaced donor atoms. The donor atoms of the bridges may all be O, N, or S, or the compounds may be mixed donor macrocycles in which the

bridge strands contain combinations of such donor atoms. Suitable cryptands include bicyclic molecules that result from joining nitrogen bridgeheads with chains of (-OCH_2CH_2-) groups, for example as in [2.2.2]cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, available under the brand names Kryptand 222 and Kryptofix 222).

Onium salts that may be used as catalysts in the base-mediated process of the step (b) include quaternary phosphonium salts and quaternary ammonium salts, which may be represented by the formulae $R^1R^2R^3R^4P^+Z^-$ and $R^1R^2R^3R^4N^+Z^-$, respectively. In these formulae, each of R^1, R^2, R^3 and R^4 typically represent, independently, a C_{1-10} alkyl group, an aryl group (e.g. phenyl, naphthyl or pyridinyl) or an arylalkyl group (e.g. benzyl or C_{1-10} alkyl-substituted phenyl), and Z^- is a halide or other suitable counterion (e.g. hydrogen sulphate).

Specific examples of such phosphonium salts and quaternary ammonium salts include tetramethylammonium chloride, tetramethylammonium bromide, benzyltriethylammonium chloride, methyltrioctylammonium chloride (available commercially under the brands Aliquat 336 and Adogen 464), tetra-n-butylammonium chloride, tetra-n-butylammonium bromide, tetra-n-butylammonium hydrogen sulphate, tetra-n-butylphosphonium chloride, tetraphenylphosphonium bromide, tetraphenylphosphonium chloride, triphenylmethylphosphonium bromide and triphenylmethylphosphonium chloride. Benzyltriethylammonium chloride is preferred for use under strongly basic conditions.

Other useful onium salts include those exhibiting high temperature stabilities (e.g. up to about 200 °C), for example 4-dialkylaminopyridinium salts, tetraphenylarsonium chloride, bis[tris(dimethylamino)phosphine]iminium chloride and tetrakis[tris(dimethylamino)phosphinimino]phosphonium chloride. The latter two compounds are also reported to be stable in the presence of hot, concentrated sodium hydroxide and, therefore, can be particularly useful.

Polyalkylene glycol compounds useful as phase transfer catalysts may be represented by the formula $R^6O(R^5O)_mR^7$ wherein R^5 is a C_{1-10} alkylene group, each of R^6 and R^7 are, independently H, a C_{1-10} alkyl group, an aryl group (e.g. phenyl, naphthyl or pyridinyl) or an arylalkyl group (e.g. benzyl or C_{1-10} alkyl-substituted phenyl), and m is an integer of at least 2. Preferable both R^6 and R^7 are the same, for example they may both by H.

Such polyalkylene glycols include diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, diisopropylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol and tetramethylene glycol, monoalkyl glycol ethers such as monomethyl, monoethyl, monopropyl and monobutyl ethers of such glycols, dialkyl ethers such as tetraethylene glycol dimethyl ether and pentaethylene glycol dimethyl ether, phenyl ethers, benzyl ethers of such glycols, and polyalkylene glycols such as polyethylene glycol (average molecular weight about 300) and polyethylene glycol (average molecular weight about 400) and the dialkyl (e.g. dimethyl, dipropyl, dibutyl) ethers of such polyalkylene glycols.

Combinations of phase transfer catalysts from within one of the groups described above may also be useful as well as combinations or mixtures from more than one group. Crown ethers and quaternary ammonium salts are the currently preferred groups of catalysts, for example 18-crown-6 and its fluorinated derivatives and benzyltriethylammonium chloride.

By the term "zinc/chromia catalyst" we mean any catalyst comprising chromium or a compound of chromium and zinc or a compound of zinc. Such catalysts are known in the art, see for example EP-A-0502605, EP-A-0773061, EP-A-0957074 and WO 98/10862, which are incorporated by reference herein. However, the present inventors have surprisingly found that zinc/chromia catalysts may be used promote the fluorination of 243db to produce the compound of formula CF_3CHFCH_2X and, optionally, to promote the dehydrohalogenation of the compound of formula CF_3CHFCH_2X to produce 1234yf. The combined fluorination/dehydrohalogenation to produce 1234yf starting from 243db in the presence of a zinc/chromia catalyst is particularly unexpected.

Typically, the chromium or compound of chromium present in the zinc/chromia catalysts of the invention is an oxide, oxyfluoride or fluoride of chromium such as chromium oxide.

The total amount of the zinc or a compound of zinc present in the zinc/chromia catalysts of the invention is typically from about 0.01% to about 25%, preferably 0.1% to about 25%, conveniently 0.01% to 6% zinc, and in some embodiments preferably 0.5% by weight to about 25 % by weight of the catalyst, preferably from about 1 to 10 % by weight of the catalyst, more preferably from about 2 to 8 % by weight of the catalyst, for example about 4 to 6 % by weight of the catalyst.

In other embodiments, the catalyst conveniently comprises 0.01% to 1%, more preferably 0.05% to 0.5% zinc.

The preferred amount depends upon a number of factors such as the nature of the chromium or a compound of chromium and/or zinc or a compound of zinc and/or the way in which the catalyst is made. These factors are described in more detail hereinafter.

It is to be understood that the amount of zinc or a compound of zinc quoted herein refers to the amount of elemental zinc, whether present as elemental zinc or as a compound of zinc.

The zinc/chromia catalysts used in the invention may include an additional metal or compound thereof. Typically, the additional metal is a divalent or trivalent metal, preferably selected from nickel, magnesium, aluminium and mixtures thereof. Typically, the additional metal is present in an amount of from 0.01 % by weight to about 25 % by weight of the catalyst, preferably from about 0.01 to 10 % by weight of the catalyst. Other embodiments may comprise at least about 0.5 % by weight or at least about 1 % weight of additional metal.

The zinc/chromia catalysts used in the present invention may be amorphous. By this we mean that the catalyst does not demonstrate substantial crystalline characteristics when analysed by, for example, X-ray diffraction.

Alternatively, the catalysts may be partially crystalline. By this we mean that from 0.1 to 50 % by weight of the catalyst is in the form of one or more crystalline compounds of chromium and/or one or more crystalline compounds of zinc. If a partially crystalline catalyst is used, it preferably contains from 0.2 to 25 % by weight, more preferably from 0.3 to 10 % by weight, still more preferably from 0.4 to 5 % by weight of the catalyst in the form of one or more crystalline compounds of chromium and/or one or more crystalline compounds of zinc.

During use in a fluorination/dehydrohalogenation reaction the degree of crystallinity may change. Thus it is possible that a catalyst of the invention that has a degree of crystallinity as defined above before use in a fluorination/dehydrohalogenation reaction and will have a degree of crystallinity outside these ranges during or after use in a fluorination/dehydrohalogenation reaction.

The percentage of crystalline material in the catalysts of the invention can be determined by any suitable method known in the art. Suitable methods include X-ray diffraction (XRD) techniques. When X-ray diffraction is used the amount of crystalline material such as the amount of crystalline chromium oxide can be determined with reference to a known amount of graphite present in the catalyst (eg the graphite used in producing catalyst pellets) or more preferably by comparison of the intensity of the XRD patterns of the sample materials with reference materials prepared from suitable internationally recognised standards, for example NIST (National Institute of Standards and Technology) reference materials.

The zinc/chromia catalysts of the invention typically have a surface area of at least 50 m^2/g and preferably from 70 to 250 m^2/g and most preferably from 100 to 200 m^2/g before it is subjected to pre-treatment with a fluoride containing species such as hydrogen fluoride or a fluorinated hydrocarbon. During this pre-treatment, which is described in more detail hereinafter, at least some of the oxygen atoms in the catalyst are replaced by fluorine atoms.

The zinc/chromia catalysts of the invention typically have an advantageous balance of levels of activity and selectivity. Preferably, they also have a degree of chemical robustness that means that they have a relatively long working lifetime. The catalysts of the invention preferably also have a mechanical strength that enables relatively easy handling, for example they may be charged to reactors or discharged from reactors using known techniques.

The zinc/chromia catalysts of the invention may be provided in any suitable form known in the art. For example, they may be provided in the form of pellets or granules of appropriate size for use in a fixed bed or a fluidised bed. The catalysts may be supported or unsupported. If the catalyst is supported, suitable supports include AlF_3, fluorinated alumina or activated carbon.

The zinc/chromia catalysts of the invention include promoted forms of such catalysts, including those containing enhanced Lewis and/or Brönsted acidity and/or basicity.

The amorphous catalysts which may be used in the present invention can be obtained by any method known in the art for producing amorphous chromia-based catalysts. Suitable

methods include co-precipitation from solutions of zinc and chromium nitrates on the addition of ammonium hydroxide. Alternatively, surface impregnation of the zinc or a compound thereof onto an amorphous chromia catalyst can be used.

Further methods for preparing the amorphous zinc/chromia catalysts include, for example, reduction of a chromium (VI) compound, for example a chromate, dichromate, in particular ammonium dichromate, to chromium (III), by zinc metal, followed by co-precipitation and washing; or mixing as solids, a chromium (VI) compound and a compound of zinc, for example zinc acetate or zinc oxalate, and heating the mixture to high temperature in order to effect reduction of the chromium (VI) compound to chromium (III) oxide and oxidise the compound of zinc to zinc oxide.

The zinc may be introduced into and/or onto the amorphous chromia catalyst in the form of a compound, for example a halide, oxyhalide, oxide or hydroxide depending at least to some extent upon the catalyst preparation technique employed. In the case where amorphous catalyst preparation is by impregnation of a chromia, halogenated chromia or chromium oxyhalide, the compound is preferably a water-soluble salt, for example a halide, nitrate or carbonate, and is employed as an aqueous solution or slurry. Alternatively, the hydroxides of zinc and chromium may be co-precipitated (for example by the use of a base such as sodium hydroxide or ammonium hydroxide) and then converted to the oxides to prepare the amorphous catalyst. Mixing and milling of an insoluble zinc compound with the basic chromia catalyst provides a further method of preparing the amorphous catalyst precursor. A method for making amorphous catalyst based on chromium oxyhalide comprises adding a compound of zinc to hydrated chromium halide.

The amount of zinc or a compound of zinc introduced to the amorphous catalyst precursor depends upon the preparation method employed. It is believed that the working catalyst has a surface containing cations of zinc located in a chromium-containing lattice, for example chromium oxide, oxyhalide, or halide lattice. Thus the amount of zinc or a compound of zinc required is generally lower for catalysts made by impregnation than for catalysts made by other methods such as co-precipitation, which also contain the zinc or a compound of zinc in non-surface locations.

Any of the aforementioned methods, or other methods, may be employed for the preparation of the amorphous catalysts which may be used in the process of the present invention.

The zinc/chromia catalysts described herein are typically stabilised by heat treatment before use such that they are stable under the environmental conditions that they are exposed to in use. This stabilisation is often a two-stage process. In the first stage, the catalyst is stabilised by heat treatment in nitrogen or a nitrogen/air environment. In the art, this stage is often called "calcination". Fluorination catalysts are then typically stabilised to hydrogen fluoride by heat treatment in hydrogen fluoride. This stage is often termed "pre-fluorination".

By careful control of the conditions under which these two heat treatment stages are conducted, crystallinity can be induced into the catalyst to a controlled degree.

For example, an amorphous catalyst may be heat treated at a temperature of from about 300 to about 600 °C, preferably from about 400 to 600 °C, more preferably from 500 to 590 °C, for example 520, 540, 560 or 580 °C for a period of from about 1 to about 12 hours, preferably for from about 2 to about 8 hours, for example about 4 hours in a suitable atmosphere. Suitable atmospheres under which this heat treatment can be conducted include an atmosphere of nitrogen or an atmosphere having an oxygen level of from about 0.1 to about 10 %v/v in nitrogen. Other oxidizing environments could alternatively be used. For example, environments containing suitable oxidizing agents include, but are not limited to, those containing a source of nitrate, CrO_3 or O_2 (for example air). This heat treatment stage can be conducted in addition to or instead of the calcining stage that is typically used in the prior art to produce amorphous catalysts.

Conditions for the pre-fluorination stage can be selected so that they do not substantially introduce crystallinity into the catalyst. This may be achieved by heat treatment of the catalyst precursor at a temperature of from about 200 to about 500 °C, preferably from about 250 to about 400 °C at atmospheric or super atmospheric pressure for a period of from about 1 to about 16 hours in the presence of hydrogen fluoride, optionally in the presence of another gas such as nitrogen.

Conditions for the pre-fluorination stage can be selected so that they induce a change in the crystallinity of the catalyst or so that they do not induce such a change. The present

inventors have found that heat treatment of the catalyst precursor at a temperature of from about 250 to about 500 °C, preferably from about 300 to about 400 °C at atmospheric or super atmospheric pressure for a period of from about 1 to about 16 hours in the presence of hydrogen fluoride, optionally in the presence of another gas such as air, can produce a catalyst in which the crystallinity is as defined above, for example from 0.1 to 8.0 % by weight of the catalyst (typically from 0.1 to less than 8.0 % by weight of the catalyst) is in the form of one or more crystalline compounds of chromium and/or one or more crystalline compounds of the at least one additional metal.

The skilled person will appreciate that by varying the conditions described above, such as by varying the temperature and/or time and/or atmosphere under which the heat treatment is conducted, the degree of crystallinity of the catalyst may be varied. Typically, for example, catalysts with higher degrees of crystallinity (e.g. from 8 to 50 % by weight of the catalyst) may be prepared by increasing the temperature and/or increasing the calcination time and/or increasing the oxidising nature of the atmosphere under which the catalyst pre-treatment is conducted.

The variation of catalyst crystallinity as a function of calcination temperature, time and atmosphere is illustrated by the following table showing a series of experiments in which 8 g samples of a 6 % zinc/chromia catalyst were subjected to calcination across a range of conditions and the level of crystallinity induced determined by X-Ray diffraction.

Calcination Time (t, hrs)	Calcination Temperature (T, °C)	Atmosphere nitrogen:air (D, v/v)	% Cryst Cr_2O_3 Content
4	400.0	15	1
4	400.0	15	1
2	450.0	20	9
6	350.0	20	0
2	450.0	10	18
2	350.0	10	0
6	450.0	20	20
6	350.0	10	0
6	450.0	10	30
4	400.0	15	1

2	350.0	20	0

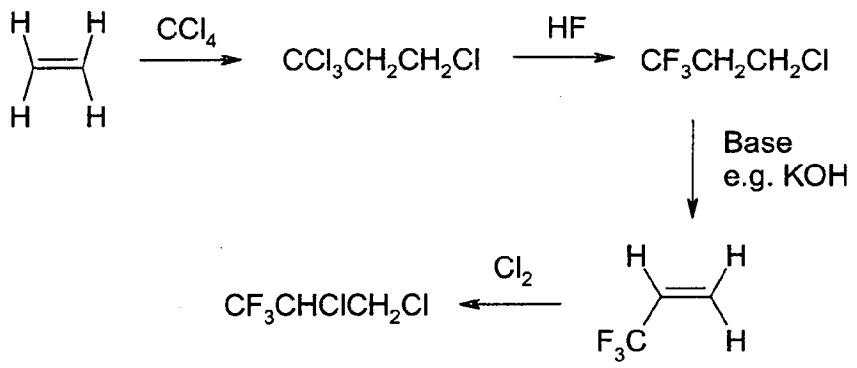
The pre-fluorination treatment typically has the effect of lowering the surface area of the catalyst. After the pre-fluorination treatment the catalysts of the invention typically have a surface area of 20 to 200 m^2/g, such as 50 to 150 m^2/g, for example less than about 100m^2/g.

In use, the zinc/chromia catalyst may be regenerated or reactivated periodically by heating in air at a temperature of from about 300 °C to about 500 °C. Air may be used as a mixture with an inert gas such as nitrogen or with hydrogen fluoride, which emerges hot from the catalyst treatment process and may be used directly in fluorination processes employing the reactivated catalyst. Alternatively, the catalyst can be regenerated continuously whilst in use by introducing an oxidising gas into the reactor e.g. oxygen or chlorine.

1,1,1-trifluoro-2,3-dichloropropane (243db) is commercially available (e.g. from Apollo Scientific Ltd, UK). Alternatively, 243db may also be prepared *via* a synthetic route starting from the cheap feedstocks carbon tetrachloride (CCl_4) and ethylene (see the reaction scheme set out below). These two starting materials may be telomerised to produce 1,1,1,3-tetrachloropropane (see, for example, J. Am. Chem. Soc. Vol. 70, p2529, 1948, which is incorporated herein by reference) (also known as HCC-250fb, or simply 250fb).

250fb may then be fluorinated to produce 3,3,3-trifluoropropene (1243zf) and/or 1,1,1-trifluoro-3-chloropropane (e.g. using HF, optionally in the presence of a chromia-containing catalyst, preferably a zinc/chromia catalyst as described herein). Dehydrohalogenation of 1,1,1-trifluoro-3-chloropropane (e.g. using NaOH or KOH) produces 3,3,3-trifluoropropene (1243zf). Alternatively, 250fb may be dehydrochlorinated to 3,3,3-trichloropropene, followed by fluorination to 1243zf.

1243zf may then be readily halogenated, such as chlorinated (e.g. with chlorine) to produce 1,1,1-trifluoro-2,3-dichloropropane (243db). This reaction scheme is summarised below (minus the route from 250fb to 1243zf *via* 3,3,3-trichloropropene).



Thus, in another aspect of the invention, there is provided a process for preparing 1234yf, the process comprising:

(i) telomerising ethylene and carbon tetrachloride (CCl_4) to produce 1,1,1,3-tetrachloropropane (250fb);

(ii) converting 250fb to 3,3,3-trifluoropropene (1243zf);

(iii) contacting 1243zf with a compound of formula AB to produce a compound of formula CF_3CHACH_2B, wherein A and B represent, independently, H, F, Cl, Br or I, provided that A and B are not both H or F;

(iv) contacting the compound of formula CF_3CHACH_2B with hydrogen fluoride (HF) in the presence of a zinc/chromia catalyst to produce a compound having the formula CF_3CHFCH_2X, wherein X is Cl or F; and

(v) dehydrohalogenating the compound of formula CF_3CHFCH_2X to produce 1234yf.

Step (i) of the above process typically comprises contacting ethylene with CCl_4 in the liquid and/or vapour phase in presence of a catalyst under conditions suitable to produce 250fb.

Any suitable catalyst may be used in step (i), such as a catalyst which comprises iron, copper and/or peroxide.

Catalysts which comprise peroxide include benzoyl peroxide and di-*t*-butyl peroxide. Catalysts which comprise iron include iron powder and ferric/ferrous halides (e.g. chlorides). Catalysts which comprise copper include salts of copper such as copper halides (e.g. $CuCl_2$), copper sulphate and/or copper cyanide.

Typically, the catalysts which comprise copper and iron are used with a co-catalyst or ligand. Suitable co-catalysts include triethylorthoformate ($HC(OEt)_3$), nitrogen/phosphorus-containing ligands, and/or ammonium/phosphonium salts. Preferred nitrogen-containing ligands include amines (e.g. primary and secondary amines), nitriles and amides. Preferred phosphorus containing ligands include phosphates, phosphites (e.g. triethylphosphite) and phosphines. Preferred ammonium and phosphonium salts include ammonium and phosphonium halides (e.g. chlorides).

The catalyst for step (i) typically is used in an amount from about 0.01 to about 50 mol % (e.g. about 0.1 to about 10 %), based on the molar sum of CCl_4 and ethylene present. An excess of the carbon tetrachloride over ethylene generally is used. For example, the molar ratio of CCl_4:C_2H_4 typically is from about 1:1 to about 50:1, such as from about 1.1:1 to about 20:1, for example from about 1.2:1 to about 10:1 or about 1.5:1 to about 5:1.

The reaction temperature for step (i) typically is within the range of from about 20 to about 300 °C, preferably from about 30 to about 250 °C, such as from about 40 to about 200 °C, e.g. from about 50 to about 150 °C.

The reaction pressure for step (i) typically is within the range of from 0 to about 40 bara, preferably from about 1 to about 30 bara.

The reaction time for step (i) generally is from about 1 second to about 100 hours, preferably from about 10 seconds to about 50 hours, such as from about 1 minute to about 10 hours.

Step (i) can be carried out in any suitable apparatus, such as a static mixer, a tubular reactor, a stirred tank reactor or a stirred vapour-liquid disengagement vessel. Step (i) may be carried out batch-wise or continuously. Preferably, the 1,1,1,3-tetrachloropropane formed in step (i) is purified and/or isolated before it is fluorinated in step (ii). The purification may be achieved by separation of the 250fb from any other products or reagents by one or more distillation, condensation or phase separation steps and/or by scrubbing with water or aqueous base.

The conversion of 250fb to 1243zf in step (ii) above typically involves fluorination and dehydrohalogenation sub-steps.

For example, 250fb may be fluorinated to produce a compound of formula $CF_3CH_2CH_2Cl$ (253fb), followed by dehydrohalogenation of 253fb to produce 1243zf. This will be referred to hereinafter as route (ii1).

Alternatively, 250fb may be dehydrochlorinated to produce 3,3,3-trichloropropene, followed by fluorination to produce 1243zf. This will be referred to hereinafter as route (ii2).

Either or both routes (ii1) and (ii2) may be used to convert 250fb to 1243zf, depending on the choice of reagents and/or catalysts. The route taken and the number of steps involved may depend on factors such as the reaction conditions and the nature of catalyst employed (if any). Such factors are described in more detail below.

In route (ii1), for example, 250fb may be fluorinated with HF in the presence of a catalyst to produce 253fb . Any suitable catalyst for HF fluorination may be used, such as compounds comprising aluminium (e.g. alumina-based catalysts) and/or chromium (e.g. chromia-based catalysts, especially zinc/chromia catalysts as described herein) and/or metal halides such as chlorides or fluorides (e.g. TaX_5, SbX_5, SnX_4, TiX_4, $FeCl_3$, NbX_5, VX_5, AlX_3, wherein X = F or Cl) and/or nitrogen-containing bases (e.g. amines and nitrogen-containing heterocycles such as pyridine). Examples of catalysts compounds comprising aluminium include AlF_3, optionally mixed with one or more transition metal compounds.

253fb may then be dehydrohalogenated to 1243zf by any suitable method, for example by base-mediated (e.g. using a base comprising alkali or alkaline earth metal hydroxides or amides), thermal or metal catalysed (e.g. zinc/chromia catalysed) dehydrohalogenation. The dehydrohalogenation may be conducted in the presence or absence of HF. Suitable reaction conditions for the dehydrohalogenation of 253fb are described hereinbefore in relation to the dehydrohalogenation step (b) of a compound of formula CF_3CHFCH_2X (wherein X = Cl or F).

The fluorination and dehydrohalogenation reactions in route (ii1) using HF may be conducted simultaneously (i.e. in a one-pot process) or sequentially, optionally with separation/isolation of the 253fb prior to dehydrohalogenation. Preferably, route (ii1) is carried out in one-pot using a zinc/chromia catalyst.

In route (ii2), the dehydrochlorination and fluorination reactions may be carried out under substantially the same reaction conditions, i.e. in a one-pot process. Thus, 250fb may be contacted with HF in the presence of a catalyst to produce 1243zf, typically *via* 253fb. Suitable catalysts include the catalysts described above in relation to route (ii1), particularly zinc/chromia catalysts.

Although HF is described as a suitable fluorination agent for step (ii), any suitable fluorination agent may be used. For example, in an alternative embodiment, 3,3,3-trifluoropropene may be produced in one pot by treating 1,1,1,3-tetrachloropropane with NaF, KF, or amine:HF complexes such as Olah's reagent.

Typically, step (ii) is carried out at a temperature of about 20 to about 500 °C. For example, when using KF or Olah's reagent (pyrindinium poly(HF)), temperatures of about 50 to about 200 °C may be used. Alternatively, when using HF, higher temperatures may be employed, such as from about 100 to about 500 °C (e.g. about 120 to about 400 °C or about 150 to about 250 °C).

The temperature used may vary depending on the nature of the catalyst employed. For example, when a nitrogen-containing base is used, the preferred temperature may range from about 100 to about 250 °C, whereas when a catalyst based on a compound of aluminium is employed, the preferred temperature may vary from about 200 to about 350 °C. When a zinc/chromia catalyst is used for step (ii), the temperature typically ranges from about 150 to about 400 °C, such as from about 150 to about 350 °C, e.g. from about 150 to about 300 °C or from about 150 to about 250 °C.

The reaction pressure for step (ii) typically is within the range of from 0 to about 30 bara, preferably from about 1 to about 20 bara.

An excess of the fluorination agent is generally used in step (ii), whether the 3,3,3-trifluoropropene is produced *via* route (ii1) or route (ii2). For example, when using HF as the fluorination agent, a molar ratio of HF: organics of from about 1:1 to about 100:1, such as from about 3:1 to about 50:1, e.g. from about 6:1 to about 30:1 may be used.

The reaction time for step (ii) generally is from about 1 second to about 100 hours, preferably from about 10 seconds to about 50 hours, such as from about 1 minute to

about 10 hours. In a continuous process, typical contact times of the catalyst with the reagents is from about 1 to about 1000 seconds, such from about 1 to about 500 seconds or about 1 to about 300 seconds or about 1 to about 50, 100 or 200 seconds.

Step (ii) can be carried out in any suitable apparatus, such as a static mixer, a tubular reactor, a stirred tank reactor or a stirred vapour-liquid disengagement vessel. Step (ii) may be carried out batch-wise or continuously. Preferably, the 1243zf formed in step (ii) is purified and/or isolated before it is reacted in step (iii). The purification may be achieved by separation of the 1243zf from any other products or reagents by one or more distillation, condensation or phase separation steps and/or by scrubbing with water or aqueous base.

Step (ii) is described in more detail towards the end of this specification in a further embodiment denoted the 1243zf preparation process.

Step (iii) is the halogenation of 1243zf and comprises contacting 1243zf with a compound of formula AB to produce a compound of formula CF_3CHACH_2B, wherein A and B represent, independently, H, F, Cl, Br or I, provided that A and B are not both H or F. Any suitable halogenating agent AB may be used in step (iii) to convert 1243zf to the compound of formula CF_3CHACH_2B . Examples include Cl_2, Br_2, I_2, ClF, ClBr, and ICl, each optionally in the presence of HF. Preferably, at least one of A or B is Cl and, therefore, 1243zf may be chlorinated by contacting it with Cl_2, ClF, ClBr and/or ICl. Chlorine (Cl_2) is a preferred chlorinating agent. Preferably, step (iii) is carried out by contacting 1243zf with chlorine (Cl_2) to produce 243db.

Step (iii) is advantageously carried out in the presence of a catalyst. Any suitable catalyst may be used, including catalysts comprising a transition metal (e.g. Ti, V, Cr, Mn, Fe, Co, Ni, Sn, Ta, Sb, Au, Ag, Mo, Ru, Rh, Pd, Pt or compounds thereof or mixtures of the foregoing) or a main group element such as carbon, silicon or aluminium or compounds thereof or mixtures of the foregoing. A preferred group of chlorination catalysts are those comprising activated carbon, alumina and/or an oxide of a transition metal.

For the avoidance of doubt, by a catalyst which comprises activated carbon, alumina and/or an oxide of a transition metal, we include catalysts that are essentially only activated carbon, alumina and/or an oxide of a transition metal and catalysts that are

activated carbon, alumina and/or an oxide of a transition metal modified, for example, by the addition of one or more metals (e.g. transition metals) and/or compounds thereof.

By "activated carbon", we include any carbon with a relatively high surface area such as from about 50 to about 3000 m^2 or from about 100 to about 2000 m^2 (e.g. from about 200 to about 1500 m^2 or about 300 to about 1000 m^2). The activated carbon may be derived from any carbonaceous material, such as coal (e.g. charcoal), nutshells (e.g. coconut) and wood. Any form of activated carbon may be used, such as powdered , granulated and pelleted activated. Activated carbon which has been modified (e.g. impregnated) by the addition of Cr, Mn, Au, Fe, Sn, Ta, Ti, Sb, Al, Co, Ni, Mo, Ru, Rh, Pd and/or Pt and/or a compound (e.g. a halide) of one or more of these metals may be used.

Alumina which has been modified by the addition of Cr, Mn, Fe, Sn, Ta, Ti, Sb, Al, Co, Ni, Mo, Ru, Rh, Pd and/or Pt and/or a compound (e.g. a halide) of one or more of these metals may be used.

An oxide of a transition metal that has been modified by the addition of Cr, Mn, Au, Fe, Sn, Ta, Ti, Sb, Al, Co, Ni, Mo, Ru, Rh, Pd and/or Pt and/or a compound (e.g. a halide) of one or more of these metals may be used.

A preferred oxide of a transition metal is an oxide of Cr, Ti, V, Zr, or Fe. For example, chromia (Cr_2O_3) alone, or chromia that has been modified by the addition of Zn, Mn, Zr, Ni, Al and/or Mg and/or a compound of one or more of these metals may be used. Suitable chromia-based catalysts include those described in EP-A-0502605, EP-A-0773061, EP-A-957074, WO 98/10862 and WO 2006/106353. A preferred chromia-based catalyst is a zinc/chromia catalyst.

Activated carbon is currently a preferred catalyst for step (iii) because, for example, it is cheap, effective and robust. Activated carbon is commercially available, e.g. from Sutcliffe-Speakman.

Step (iii) may be conducted in the vapour or liquid phase, preferably in the vapour phase. Step (iii) may be carried in the liquid phase using the 243db product as the solvent. The heat of reaction in such a process may be removed by boiling off the 243db product/solvent.

Typically, step (iii) is conducted at a temperature of from about -100 to about 400 °C, such as from about -80 to about 300 °C or -50 to about 250 °C, e.g. from about 0 to about 200 °C or about 50 to about 150 °C. The process may be conducted at a pressure of from about 0 to about 30 bara, such as from about 0.1 to about 20 bara or from about 0.5 to about 10 bara, e.g. from about 1 to about 5 bara.

Step (iii) can be carried out in any suitable apparatus, such as a static mixer, a tubular reactor, a stirred tank reactor or a stirred vapour-liquid disengagement vessel. Step (iii) may be carried out batch-wise or continuously.

The reaction time for step (iii) generally is from about 1 second to about 100 hours, preferably from about 10 seconds to about 50 hours, such as from about 1 minute to about 10 hours.

Typically, the molar ratio of 1243zf:compound of formula AB (e.g. Cl_2) in step (iii) is from about 10:1 to about 1:5, such as from about 5:1 to about 1:2, for example from about 3:1 to about 1.5:1 (e.g. about 2.5:1 to about 1:1).

The compound of formula CF_3CHACH_2B (e.g. 243db) formed in step (iii) may be purified and/or isolated before being used in step (iv). For example, the compound of formula CF_3CHACH_2B may be separated (e.g. by distillation, condensation and phase separation, and/or scrubbing with water or aqueous base) from the compound of formula AB and 1243zf in step (iii) and transferred to a different reaction vessel or zone for conducting the fluorination step (iv).

In this way, the reaction conditions (e.g. temperature and pressure) used in step (iii) and (iv) can be optimised to facilitate the halogenation and fluorination reactions, respectively. For example, it is currently thought to be optimal to use higher temperature and/or pressure conditions in the fluorination step (iv) compared to the halogenation step (iii).

In another embodiment, step (iii) may be combined with step (iv), i.e. these steps may be carried out simultaneously in a one-pot process. This combined process (referred to hereinafter as process (x)) comprises contacting 3,3,3-trifluoropropene (1243zf) with a compound of formula AB selected from Cl_2, Br_2, I_2, ClF, ClBr, and ICl and HF in the presence of a zinc/chromia catalyst to produce a compound of formula CF_3CHFCH_2X,

wherein X is Cl or F. Thus, in process (x), the zinc/chromia catalyst acts as both a chlorination and fluorination catalyst. Chlorine (Cl_2) is a preferred compound of formula AB in process (x).

In process (x), the conditions used (e.g. temperature, pressure and molar ratio of 1243:chlorine) fall within the broadest ranges set out above in relation to the halogenation of 1243zf to the compound of formula CF_3CHACH_2B (e.g. 243db) (i.e. step (iii) alone). However, the simultaneous chlorination/hydrofluorination in process (x) may require a higher temperature compared to the corresponding halogenation (e.g. chlorination) alone defined in step (iii). For example, preferred temperature conditions for process (x) typically range from about 50 to about 400 °C, such as from about 100 to about 350 °C.

Typically, HF will be used in a molar excess compared to the amount of 1243zf and/or chlorine in process (x). For example, the molar ratio of HF:1243zf may be in the range of from about 1:1 to about 200:1, such as from about 2:1 to about 150:1, e.g. from about 5:1 to about 100:1.

As described hereinbefore, steps (a) and (b) may be conducted in a one-pot process. Steps (a) and (b) correspond to steps (iv) and (v). Thus, steps (iii), (iv) and (v) may also be carried out simultaneously, and in a further aspect of the invention, there is provided a process for preparing 1234yf comprising contacting 3,3,3-trifluoropropene (1243zf) with chlorine a compound of formula AB and HF in the presence of a zinc/chromia catalyst to produce 1234yf, wherein A and B represent, independently, H, F, Cl, Br or I, provided that A and B are not both H or F. This will be referred to hereinafter as process (y).

Any suitable halogenating agent of formula AB may be used in process (y). Examples include Cl_2, Br_2, I_2, ClF, ClBr, and ICl. Preferably, at least one of A or B is Cl and, therefore, 1243zf is chlorinated by contacting it with Cl_2, ClF, ClBr and/or ICl. Chlorine (Cl_2) is a preferred chlorinating agent.

In this process, the zinc/chromia catalyst acts as a chlorination, fluorination and dehydrohalogenation catalyst.

Process (y) may be carried out in the liquid or vapour phase and at a temperature of from about -100 to about 400 °C, such as from about 0 to about 390 °C or about 100 to about

350 °C, e.g. about 150 to about 300 °C. A pressure of from 0 to about 30 bara may be used in process (y), such as from about 0.1 to about 25 bara or about 0.5 to about 20 bara, e.g. from about 1 to about 20 bara.

Typically, the molar ratio of 1243zf:compound of formula AB (e.g. Cl_2) in process (y) is from about 10:1 to about 1:5, such as from about 5:1 to about 1:2, for example from about 3:1 to about 1.5:1 (e.g. about 2.5:1 to about 1:1). The molar ratio of HF:organics is typically in the range of from about 0.1:1 to about 100:1, such as from about 0.5:1 to about 50:1 or about 1:1 to about 40:1, e.g. from about 2:1 to about 30:1 or from about 5:1 to about 20:1.

Typically, the 1234yf formed in process (y) is purified. This may be achieved by conventional methods, such as by distillation, condensation, phase separation and/or scrubbing (e.g. with water or aqueous base).

In a further embodiment, the subject invention provides a process for preparing 3,3,3-trifluoropropene (1243zf), the process comprising contacting a compound of formula $CX_3CH_2CH_2X$ or $CX_3CH=CH_2$, with hydrogen fluoride (HF) in the presence of a zinc/chromia catalyst, wherein each X independently is F, Cl, Br or I, provided that in the compound of formula $CX_3CH=CH_2$, at least one X is not F. Unless otherwise stated, this will be referred to hereinafter as the 1243zf preparation process (of the invention).

In a preferred embodiment, this process relates to the reaction of a compound of formula $CX_3CH_2CH_2X$ to produce 1243zf.

The compound of formula $CX_3CH_2CH_2X$ represents any halopropane wherein X = F, Cl, Br or I. In a preferred aspect, X = F or Cl. Examples of compounds of formula $CX_3CH_2CH_2X$ include 1,1,1,3-tetrachloropropane ($CCl_3CH_2CH_2Cl$, 250fb), 1,1,3-trichloro-1-fluoropropane ($CCl_2FCH_2CH_2Cl$), 1,3-dichloro-1,1-difluoropropane ($CClF_2CH_2CH_2Cl$), 3-chloro-1,1,1-trifluoropropane ($CF_3CH_2CH_2Cl$, 253fb) and 1,1,1,3-tetrafluoropropane ($CF_3CH_2CH_2F$, 254fb).

In one aspect, the compound of formula $CX_3CH_2CH_2X$ is selected from 250fb, 253fb and 254fb. In a preferred embodiment, the compound of formula $CX_3CH_2CH_2X$ is 253fb. In a further preferred embodiment, the compound of formula $CX_3CH_2CH_2X$ is 254fb. In a particularly preferred embodiment, the compound of formula $CX_3CH_2CH_2X$ is 250fb.

The compound of formula $CX_3CH=CH_2$ represents any halopropene wherein X = F, Cl, Br or I, provided that at least one X is not F. Preferably, X is F or Cl (provided that at least one X is not F). Examples of compounds of formula $CX_3CH=CH_2$ include 3,3,3-trichloropropene ($CCl_3CH=CH_2$), 3,3-dichloro-3-fluoropropene ($CCl_2FCH=CH_2$) and 3-chloro-3,3-difluoropropene ($CClF_2CH=CH_2$). In a preferred aspect, the compound of formula $CX_3CH=CH_2$ represents 3,3,3-trichloropropene.

The inventors have unexpectedly found that zinc/chromia catalysts are particularly effective for the fluorination and/or dehydrohalogenation reactions required by the 1243zf preparation process. In particular, the zinc/chromia catalysts are believed to be more active than other catalysts, such as chromia-based catalysts. This enables the 1243zf preparation process to be conducted using less forcing conditions (e.g. lower temperature and/or pressure) than would otherwise be necessary.

The zinc/chromia catalyst may be used in the 1243zf preparation process in an amount of from about 0.01 to about 50 % by weight, such as from about 0.1 to about 30%, for example from about 0.5 to about 20%, based on the combined weight of organics (e.g. compound of formula $CX_3CH_2CH_2X$ or $CX_3CH=CH_2$) and HF.

The 1243zf preparation process can be carried out in any suitable apparatus, such as a static mixer, a stirred tank reactor or a stirred vapour-liquid disengagement vessel. Preferably, the apparatus is made from one or more materials that are resistant to corrosion, e.g. Hastelloy® or Inconel®.

The 1243zf preparation process may be carried out batch-wise or (semi-)continuously. Preferably, the process of the invention is carried out continuously. Typically, the 1243zf preparation process is carried out in the vapour phase.

The process may be carried out at atmospheric, sub- or super atmospheric pressure, typically at from 0 to about 30 bara, preferably from about 1 to about 20 bara.

Typically, the 1243zf preparation process of the invention is carried out a temperature of from about 100 °C to about 500 °C (e.g. from about 150 °C to about 500 °C or about 100 to about 450 °C). Preferably, the process is conducted at a temperature of from about 150 °C to about 450 °C, such as from about 150 °C to about 400 °C, e.g. from about 200

°C to about 350 °C. Lower temperatures may also be used in the process of the invention, for example in the conversion of 250fb to 1243zf, such as from about 150 °C to about 350 °C, e.g. from about 150 °C to about 300 °C or from about 150 °C to about 250 °C.

The 1243zf preparation process typically employs a molar ratio of HF:organics of from about 1:1 to about 100:1, such as from about 3:1 to about 50:1, e.g. from about 4:1 to about 30:1 or about 5:1 or 6:1 to about 20:1 or 30:1.

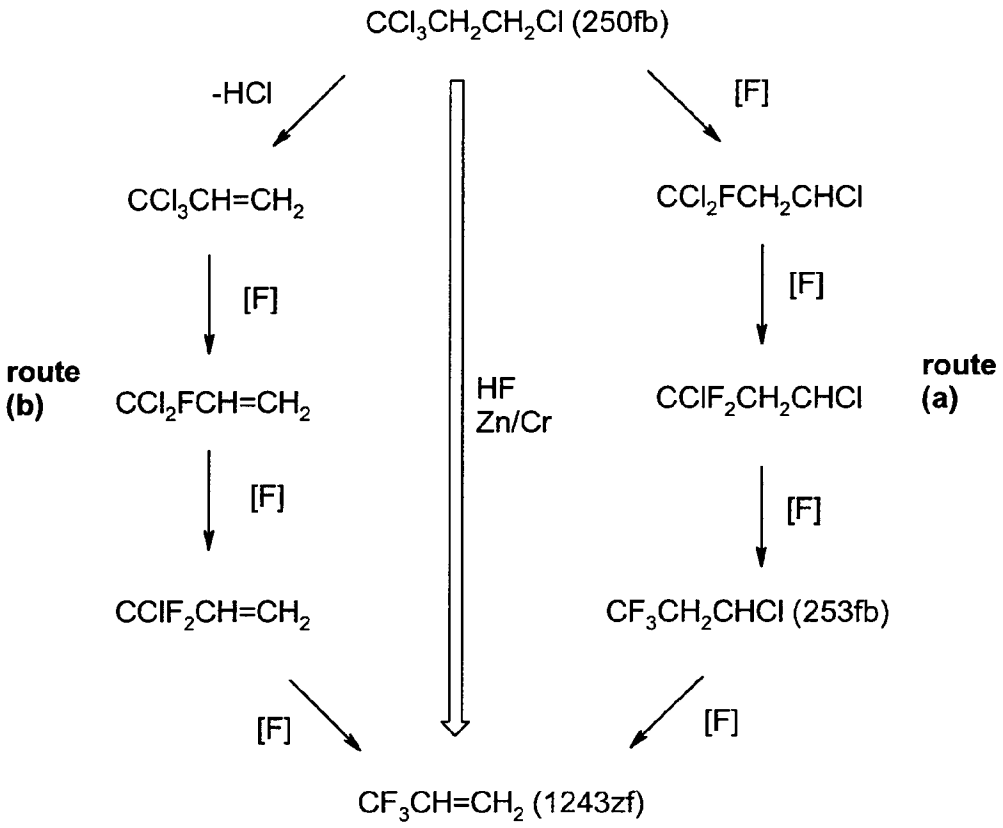
The reaction time for the 1243zf preparation process generally is from about 1 second to about 100 hours, preferably from about 10 seconds to about 50 hours, such as from about 1 minute to about 10 or 20 hours. In a continuous process, typical contact times of the catalyst with the reagents is from about 1 to about 1000 seconds, such from about 1 to about 500 seconds or about 1 to about 300 seconds or about 1 to about 50, 100 or 200 seconds.

The 1243zf preparation process is particularly effective for preparing 3,3,3-trifluoropropene (1243zf) by contacting 1,1,1,3-tetrachloropropane (250fb) with hydrogen fluoride (HF) in the presence of a zinc/chromia catalyst.

250fb may be purchased from common suppliers of halogenated hydrocarbons, such as Apollo Scientific, Stockport, UK. Alternatively, 250fb may be prepared by the telomerisation of carbon tetrachloride (CCl_4) and ethylene (see, for example, J. Am. Chem. Soc. Vol. 70, p2529, 1948, which is incorporated herein by reference).

The conversion of 250fb to 1243zf typically involves fluorination and dehydrohalogenation sub-steps.

For example, 250fb may be fluorinated to produce a compound of formula $CX_3CH_2CH_2Cl$ (wherein X = Cl or F), as illustrated in the scheme below. 1243zf may be produced by a final dehydrochlorination step of the compound of formula $CX_3CH_2CH_2Cl$ wherein X = F. This is illustrated below as route (a).



Alternatively, 250fb may be dehydrochlorinated to produce 3,3,3-trichloropropene, followed by step-wise fluorination to produce 1243zf. This is illustrated above as route (b). Routes (a) and (b) correspond to routes (ii1) and (ii2), respectively, as described herein in relation to step (ii) of the process of the invention.

Either or both routes (a) and (b) may be operable to convert 250fb to 1243zf. For example, CCl_2FCH_2CHCl in route (a) may be dehydrochlorinated to produce $CCl_2FCH=CH_2$ in route (b). It is anticipated that some of these reactions may occur spontaneously if HF and 250fb are mixed at elevated temperatures, but the reaction will not go to completion in the absence of a zinc/chromia catalyst in any reasonable timescale.

Surprisingly, the inventors have found that zinc/chromia catalysts are effective at facilitating the one-pot conversion of 250fb and HF to 1243zf. In particular, the activity of the catalyst is believed to allow less forcing conditions (e.g. lower temperatures) compared to known (vapour phase) processes for producing 1243zf, whilst maintaining excellent conversion of 250fb and selectivity to 1243zf.

The invention will now be illustrated by the following non-limiting examples.

Example 1: Single stage dehydrohalogenation of CF_3CFHCH_2F (245eb) to 1234yf

A 1.25cm (0.5") x 30 cm Inconel reactor tube loaded with 4g 5.2% zinc/chromia catalyst. The catalyst was dried under flowing nitrogen (50 ml/min) for 2 hours at 250 °C. After the drying time, HF (5-8 ml/min) was introduced into the nitrogen stream to begin fluorination of the catalyst. The temperature was ramped to 380 °C at 40 °C/min and held there for 16 hours. After 2-3 hours HF breakthrough was detected in the reactor off-gas and the nitrogen flow was switched off. After this treatment the reactor temperature was reduced to the temperatures shown in Table 1 and a mixture comprising nitrogen and 245eb passed over it. Samples of the reactor off-gas were taken and analysed by GC and GC-MS. The GC was calibrated using known standards to determine response factors and an average response factor was used to quantify unknowns.

Table 1

Nitrogen flow 8 ml/min, 245eb flow 2 ml/min									
Temperature °C / **Product**	**200**	**225**	**250**	**275**	**300**	**325**	**350**	**375**	**400**
1234yf	0.4	0.9	2.4	17.7	40.7	51.8	88.8	96.4	100.0
1243zf	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
245eb	99.2	97.2	93.2	71.2	59.2	48.2	2.9	0.0	0.0
245cb	0.2	1.7	4.3	11.1	0.0	0.0	8.2	3.6	0.0

245cb = $CF_3CF_2CH_3$

The results in Table 1 show that zinc/chromia is a surprisingly effective catalyst for the dehydrofluorination of 245eb to 1234yf.

Example 2: Preparation of 1234yf/245eb from 243db

Two Inconel reactors (30 cm x 0.5") were loaded with 6 g each of a 5.2% Zn/chromia catalyst. These tubes were then places in series and the catalyst dried under flowing nitrogen (80 ml/min) at 250°C and 3 barg pressure overnight. The catalyst was then

activated by treatment with a mixture of 4 ml/min HF and 80 ml/min nitrogen at 300°C and 3 barg pressure for a period of 72 hours. Whilst at 300°C the nitrogen flow was reduced to zero. When HF breakthrough was detected (4 hours), the temperature was ramped to 380°C at 25°C/hour and held there for a further 7 hours.

After activation the pressure was increased to 15 barg and the first reactor temperature was set to 340°C and the second set to 100°C and a feed mixture consisting of 243db (10 ml/min) and HF (100 ml/min) passed through them. The gases exiting the train of reactors were sampled and analysed by GC-MS, the results are presented below:

243db conversion 90 %
Products: 1233xf (70 %), 244 isomers including $CF_3CFClCH_3$ (10 %), 1234yf (1.4 %), 245eb (1.0 %)

Example 3: Hydrofluorination of 250fb ($CCl_3CH_2CH_2Cl$) at elevated pressure

The reactor, made from an Inconnel tube 30 cm x 0.5 inches, was charged with 6g of a 5.2 % Zn/Chromia catalyst which was essentially amorphous in character, which was treated as follows:

The catalyst was first dried by heating under nitrogen (80 ml/min) at 250°C and 3 barg for 48 hours. Next, pre-fluorination of the catalyst was begun by introducing HF (4 ml/min) into the nitrogen stream and increasing the temperature to 300°C for 16 hours. During the last 5 hours the nitrogen flow was reduced steadily to zero. The temperature was then ramped to 380°C at 25°C/hr and held at 380°C for 7 hours and then cooled to 250°C at 25°C/hr.

A feed mixture comprising 250fb (3 ml/min) and HF (45 ml/min) was then passed over the catalyst at 15 barg and 200°C. The gases exiting the reactor were periodically sampled and analysed by GC after passing through an alkaline scrubber to remove acid gases. The only products detected in the reactor off-gases following following removal of the acid gases were the desired product 1243zf (91 mol %, $CF_3CH=CH_2$) and 1,1-difluoro-1,3-dichloropropane (9 mol %, $CF_2ClCH_2CH_2Cl$).

It is believed that the 1,1-difluoro-1,3-dichloropropane could be converted to 1243zf by altering the reaction conditions (e.g. by increasing the temperature and/or contact time). In this way, 250fb could be fully converted in 100% selectivity to 1243zf in a single pass.

Example 4: Hydrofluorination of 250fb ($CCl_3CH_2CH_2Cl$) at atmospheric pressure

The reactor, made from an Inconnel tube 30 cm x 0.5 inches, was loaded with 2.0 g of a 5.2 % wt Zn on chromia catalyst which was essentially amorphous in character. The catalyst was then dried under nitrogen (80 ml/min) at 250°C for 3 hours. HF (20 ml/min) was then introduced into the nitrogen flow and pre-fluorination of the catalyst commenced. When HF was detected in the reactor off-gases the reactor temperature was ramped from 250°C to 370°C at 25°C/hr and maintained there for 7 hours before being cooled back to 200°C at 25°C/hr.

A feed mixture comprising 250fb (1 ml/min), HF (25 ml/min) and nitrogen (30 ml/min) was fed to the reactor at 200°C for a total of 15 hours. The gases exiting the reactor were scrubbed with a an alkaline solution to remove acid gases and analysed by GC-MS and GC. The only species identified in the scrubbed reactor off-gases throughout the whole experiment was 1243zf.

Examples 3 and 4 demonstrate that the reaction of 250fb with HF using a zinc/chromia catalyst selectively produces 1243zf under very mild conditions.

Example 5: Vapour phase conversion of 254fb ($CF_3CH_2CH_2F$) to 1243zf ($CF_3CH=CH_2$)

The reactor, made from an Inconnel tube 30 cm x 0.5 inches was loaded with 2.0 g of a 5.2 % wt Zn on chromia catalyst which was essentially amorphous in character. The catalyst was then dried under nitrogen (80 ml/min) at 250°C for 3 hours. HF (20 ml/min) was then introduced into the nitrogen flow and pre-fluorination of the catalyst commenced. When HF was detected in the reactor off-gases the reactor temperature was ramped from 250°C to 370°C at 25°C/hr and maintained there for 7 hours before being cooled back to 200°C at 25°C/hr.

Mixtures of HF and 254fb were then fed across the catalyst at various temperatures and ratio's to demonstrate the conversion of 254fb to 1243zf. Nitrogen carrier gas flows were

used to aid delivery of the feeds to the reactor. The gases exiting the reactor were analysed by GC-MS and GC. The results are summarised in the Table below:

Temperature (°C)	200	225	250	200	225	250	275	300	300	225	250
254fb feed (ml/min)	13.5	12.1	16.7	20.4	22.9	10.6	12.8	10.0	1.0	4.9	4.9
HF feed (ml/min)	27.9	27.9	27.6	34.3	35.3	35.4	35.2	35.6	35.3	0	0
Ratio HF:254fb	2.1	2.3	1.7	1.7	1.5	3.3	2.8	3.6	35.4	N/A	N/A
Total N_2 flow (ml/min)	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	10.1	5	5
ROG* 254fb (mol %)	93.3	50.1	14.8	93.3	71.9	17.4	1.5	0.1	0.7	1.3	0.1
ROG* 1243zf (mol %)	6.7	49.9	85.2	6.7	28.1	82.6	98.5	99.9	99.3	98.7	99.9

*ROG = Reactor Off-gas composition

As can be seen the conversion of 254fb to 1243xf is clean and facile over a zinc/chromia catalyst at moderate conditions.

Claims

1. A process for the preparation of 2,3,3,3-tetrafluoropropene (1234yf) comprising:
(a) contacting 1,1,1-trifluoro-2,3-difluoropropane (243db) with hydrogen fluoride (HF) in the presence of a zinc/chromia catalyst to produce a compound having the formula CF_3CHFCH_2X, wherein X is Cl or F; and
(b) dehydrohalogenating the compound of formula CF_3CHFCH_2X to produce 1234yf.

2. A process according to claim 1 wherein step (a) is carried out at in the vapour and/or liquid phase a temperature of from -70 to 400 °C and a pressure of from 0 to 30 bara.

3. A process according to claim 1 or 2 wherein step (b) is carried out at in the vapour and/or liquid phase a temperature of from -70 to 1000 °C and a pressure of from 0 to 30 bara.

4. A process according to any of claims 1 to 3 wherein step (b) is carried out in the presence of a zinc/chromia catalyst.

5. A process according to claim 4 wherein step (b) is carried out at a temperature of from -70 to 400 °C.

6. A process according to any of the preceding claims wherein step (a) is carried out at a pressure of from 5 to 28 bara.

7. A process according to any of the preceding claims wherein step (b) is carried out at a pressure of from 0.1 to 20 bara.

8. A process according to any of the preceding claims wherein step (b) is carried out in the presence of HF.

9. A process according to any of the preceding claims wherein step (b) is carried out in the absence of an added HF feed.

10. A process according to any of the preceding claims wherein step (b) is carried out in the presence of a diluent gas.

11. A process according to any of the preceding claims wherein the molar ratio of HF:organics in step (a) is from 1:1 to 100:1.

12. A process according to any of the preceding claims wherein the molar ratio of HF:organics in step (b) is from 0.01:1 to 50:1.

13. A process according to any of claims 1 to 3 wherein step (b) is carried out in the presence of a base.

14. A process according to claim 13 wherein step (b) is carried out at a temperature of from -50 to 300 °C.

15. A process according to claim 13 or 14 wherein the base is selected from a metal hydroxide, a metal amide and mixtures thereof.

16. A process according to any of claims 13 to 15 wherein the base is an alkali metal hydroxide.

17. A process according to claim 16 wherein the alkali metal hydroxide is selected from sodium hydroxide and potassium hydroxide.

18. A process according to any of claims 13 to 15 wherein the base is an alkaline earth metal hydroxide.

19. A process according to claim 18 wherein the alkaline earth metal hydroxide is calcium hydroxide.

20. A process according to any of claims 13 to 19 wherein step (b) is carried out in a solvent.

21. A process according to claim 20 wherein the solvent is selected from water, alcohols, diols, polyols, polar aprotic solvents and mixtures thereof.

22. A process according to claim 21 and wherein the process optionally is carried out in the presence of a co-solvent or diluent.

23. A process according to any of claims 13 to 22 wherein step (b) is carried out in the presence of a catalyst.

24. A process according to claim 23 wherein the catalyst is a crown ether.

25. A process according to claim 24 wherein the crown ether is 18-crown-6.

26. A process according to claim 23 wherein the catalyst is a quaternary ammonium salt.

27. A process according to any of claims 23 to 26 wherein the catalyst is fluorinated.

28. A process according to any of the preceding claims comprising the step (iii) of contacting 3,3,3-trifluoropropene (1243zf) with a compound of formula AB to produce a compound of formula CF_3CHACH_2B, wherein A and B represent, independently, H, F, Cl, Br or I, provided that A and B are not both H or F.

29. A process according to claim 28 comprising the step (ii) of converting 1,1,1,3-tetrachloropropane (250fb) to 3,3,3-trifluoropropene (1243zf).

30. A process according to claim 29 comprising the step (i) of telomerising ethylene and carbon tetrachloride (CCl_4) to produce the 1,1,1,3-tetrachloropropane.

31. A process for preparing 1234yf, the process comprising:

(i) telomerising ethylene and carbon tetrachloride (CCl_4) to produce 1,1,1,3-tetrachloropropane;

(ii) converting 1,1,1,3-tetrachloropropane (250fb) to 3,3,3-trifluoropropene (1243zf);

(iii) contacting 1243zf with a compound of formula AB to produce a compound of formula CF_3CHACH_2B, wherein A and B represent, independently, H, F, Cl, Br or I, provided that A and B are not both H or F;

(iv) contacting the compound of formula CF_3CHACH_2B with hydrogen fluoride (HF) in the presence of a zinc/chromia catalyst to produce a compound having the formula CF_3CHFCH_2X, wherein X is Cl or F; and

(v) dehydrohalogenating the compound of formula CF_3CHFCH_2X to produce 1234yf.

32. A process according to claim 30 or 31 wherein step (i) comprises contacting ethylene with CCl_4 in the liquid and/or vapour phase in the presence of a catalyst in an amount of from about 0.01 to about 50 mol %.

33. A process according to claim 32 wherein step (i) the catalyst comprises iron, copper and/or peroxide.

34. A process according to any of claims 30 to 33 wherein step (i) the molar ratio of CCl_4:ethylene is from about 1:1 to about 50:1.

35. A process according to any of claims 30 to 34 wherein step (i) is conducted at a temperature of from about 20 to about 300 °C and a pressure of from 0 to about 40 bara.

36. A process according to any of claims 29 to 35 wherein the 1,1,1,3-tetrachloropropane is purified before conversion to 3,3,3-trifluoropropene (1243zf).

37. A process according to any of claims 29 to 36 wherein step (ii) comprises fluorination of 1,1,1,3-tetrachloropropane to produce a compound of formula $CF_3CH_2CH_2Cl$ (253fb), followed by dehydrohalogenation of the 253fb to produce 3,3,3-trifluoropropene.

38. A process according to claim 37 wherein the fluorination comprises contacting 1,1,1,3-tetrachloropropane with HF in the presence of a catalyst to produce the 253fb.

39. A process according to claim 39 wherein the catalyst is selected from compounds comprising aluminium, compounds comprising chromium (e.g. a zinc/chromia catalyst), metal halides, nitrogen-containing bases and combinations thereof.

40. A process according to claim any of claims 37 to 39 wherein the fluorination and dehydrohalogenation reactions are conducted simultaneously.

41. A process according to claim 40 comprising contacting 1,1,1,3-tetrachloropropene with HF in the presence of a catalyst to produce 1243zf.

42. A process according to any of claims 29 to 41 wherein step (ii) is carried out at a temperature of from about 20 to about 500 °C and a pressure of from 0 to about 30 bara.

43. A process according to any of claims 38 to 42 wherein step (ii) the molar ratio of HF: organics is from about 1:1 to about 100:1.

44. A process according to any of claims 39 or 47 wherein the catalyst is activated carbon or a zinc/chromia catalyst.

45. A process according to any of claims 28 to 44 wherein step (iii) comprises contacting 1243zf with a compound of formula AB selected from Cl_2, ClF, ClBr and/or ICl.

46. A process according to claim 45 wherein the step (iii) comprises contacting 1243zf with Cl_2 to produce 1,1,1-trifluoro-2,3-dichloropropane (243db).

47. A process according to claim 45 or 46 wherein step (iii) is carried out in the presence of a catalyst.

48. A process according to claim 47 wherein the catalyst comprises activated carbon, alumina and/or an oxide of a transition metal.

49. A process according to claim 47 or 48 wherein the catalyst is activated carbon.

50. A process according to any of claims 28 to 49 wherein step (iii) is conducted at a temperature of from about -100 to about 400 °C and a pressure of from 0 to about 30 bara.

51. A process according to any of claims 28 to 50 wherein the molar ratio of 1243zf:compound of formula AB is from about 10:1 to about 1:5.

52. A process according to any of claims 31 to 50 wherein the compound of formula CF_3CHACH_2B produced in step (iii) is purified prior to step (iv).

53. A process according to claim 47 wherein steps (iii) and (iv) are conducted simultaneously in a process comprising contacting 1243zf with Cl_2 and HF in the presence of a zinc/chromia catalyst to produce a compound of formula CF_3CHFCH_2X, wherein X is Cl or F.

54. A process according to any of claims 31 to 53 wherein step (iv) the compound of formula CF_3CHACH_2B is 243db.

55. A process according to claim 54 wherein the conditions for steps (iv) and (v) are as defined in claims 1 to 27 for steps (a) and (b), respectively.

56. A process for preparing a compound of formula CF_3CHFCH_2X, wherein X is Cl or F, the process comprising contacting 3,3,3-trifluoropropene (1243zf) with a compound of formula AB selected from Cl_2, Br_2, I_2, ClF, ClBr, and ICl and HF in the presence of a zinc/chromia catalyst to produce the compound of formula CF_3CHFCH_2X.

57. A process for preparing 1234yf comprising contacting 3,3,3-trifluoropropene (1243zf) with a compound of formula ZB and HF in the presence of a zinc/chromia catalyst to produce 1234yf, wherein A and B represent, independently, H, F, Cl, Br or I, provided that A and B are not both H or F.

58. A process for preparing 3,3,3-trifluoropropene (1243zf), the process comprising contacting a compound of formula $CX_3CH_2CH_2X$ or $CX_3CH=CH_2$, with hydrogen fluoride (HF) in the presence of a zinc/chromia catalyst, wherein each X independently is F, Cl, Br or I, provided that in the compound of formula $CX_3CH=CH_2$, at least one X is not F.

59. A process according to claim 58 wherein X is F or Cl.

60. A process according to claim 58 or 59, wherein the process comprises contacting a compound of formula $CX_3CH_2CH_2X$.

61. A process according to any of claims 58 to 60 wherein the compound of formula $CX_3CH_2CH_2X$ comprises $CF_3CH_2CH_2Cl$ (253fb).

62. A process according to any of claims 58 to 61 wherein the compound of formula $CX_3CH_2CH_2X$ comprises $CCl_3CH_2CH_2Cl$ (250fb).

63. A process according to any of claims 58 to 62 wherein the process is conducted at a temperature of from about 100 °C to about 500 °C, preferably from about 150 °C to about 450 °C.

64. A process according to any of claims 58 to 63 wherein the process is conducted at a pressure of from 0 to about 30 bara, preferably from about 1 to about 20 bara.

65. A process according to any of claims 58 to 64 wherein the molar ratio of HF:organics is from about 1:1 to about 100:1, preferably from about 3:1 to about 50:1.

66. A process according to any of claims 58 to 65 wherein the process is conducted in the vapour phase.

67. A process according to any of claims 58 to 66 wherein the process is continuous or semi-continuous.

68. Any novel process generally as herein described.

69. Any novel process generally as herein described with reference to the Examples.

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13/229,016	09/09/2011	SELMA BEKTESEVIC	H0024680-4511	8706

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HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962

EXAMINER	
BROOKS, CLINTON A	

ART UNIT	PAPER NUMBER
1621	

NOTIFICATION DATE	DELIVERY MODE
01/17/2013	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

patentservices-us@honeywell.com
DL-SM-IP@Honeywell.com

Office Action Summary	Application No.	Applicant(s)	
	13/229,016	BEKTESEVIC ET AL.	
	Examiner	Art Unit	
	CLINTON BROOKS	1621	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *1* MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *09 September 2011*.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

5)☒ Claim(s) *1-46* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☐ Claim(s) _____ is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☒ Claim(s) *1-46* are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☐ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

DETAILED ACTION

Election/Restrictions

This application contains claims directed to the following patentably distinct species:

Please elect a specific fluorinated olefin, and any specific fluorinated intermediates, and specific starting materials. Please provide the claims that read on the elected species. Specific examples are provided in for example claim 10.

The species are independent or distinct because they are structurally diverse. In addition, these species are not obvious variants of each other based on the current record.

Applicant is required under 35 U.S.C. 121 to elect a single disclosed species, or a single grouping of patentably indistinct species, for prosecution on the merits to which the claims shall be restricted if no generic claim is finally held to be allowable. Currently, claim 1 and 21 are generic.

There is a search and/or examination burden for the patentably distinct species as set forth above because at least the following reason(s) apply:

In this case at least different search terms and or search queries would be required to search the full scope of the invention.

Applicant is advised that the reply to this requirement to be complete must include (i) an election of a species or a grouping of patentably indistinct species to be examined even though the requirement may be traversed (37 CFR 1.143) **and (ii) identification of the**

claims encompassing the elected species or grouping of patentably indistinct species, including any claims subsequently added. An argument that a claim is allowable or that all claims are generic is considered nonresponsive unless accompanied by an election.

The election may be made with or without traverse. To preserve a right to petition, the election must be made with traverse. If the reply does not distinctly and specifically point out supposed errors in the election of species requirement, the election shall be treated as an election without traverse. Traversal must be presented at the time of election in order to be considered timely. Failure to timely traverse the requirement will result in the loss of right to petition under 37 CFR 1.144. If claims are added after the election, applicant must indicate which of these claims are readable on the elected species or grouping of patentably indistinct species.

Should applicant traverse on the ground that the species, or groupings of patentably indistinct species from which election is required, are not patentably distinct, applicant should submit evidence or identify such evidence now of record showing them to be obvious variants or clearly admit on the record that this is the case. In either instance, if the examiner finds one of the species unpatentable over the prior art, the evidence or admission may be used in a rejection under 35 U.S.C. 103(a) of the other species.

Upon the allowance of a generic claim, applicant will be entitled to consideration of claims to additional species which depend from or otherwise require all the limitations of an allowable generic claim as provided by 37 CFR 1.141.

Applicant is reminded that upon the cancellation of claims to a non-elected invention, the inventorship must be amended in compliance with 37 CFR 1.48(b) if one or more of the currently named inventors is no longer an inventor of at least one claim remaining in the

application. Any amendment of inventorship must be accompanied by a request under 37 CFR 1.48(b) and by the fee required under 37 CFR 1.17(i).

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CLINTON BROOKS whose telephone number is (571)270-7682. The examiner can normally be reached on Monday-Friday 8:00 AM to 5:00 PM EST.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, JOHANN RICHTER can be reached on (571)272-0646. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CLINTON BROOKS/
Examiner, Art Unit 1621

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: **Selma Bektesevic, et al.** Examiner: **Clinton A. Brooks**

Application No.: **13/229,016** Conf. No. **8706** Group Art Unit: **1621**

Filed: **September 9, 2011** Attorney Docket No. **H0024680**

Title: **INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS**

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Mail Stop: Amendments
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

RESPONSE TO RESTRICTION REQUIREMENT

Sir:

This Reply is in response to the Restriction Requirement mailed January 17, 2013. A response to the Requirement is respectfully submitted herein that conforms to the submission requirements. Applicants believe that no fees are currently due to further the prosecution of this application. However, if any fees are necessary, please charge such fees to Deposit Account No. 50-1943.

Amendments to the Specification begin on page 2 of this correspondence.

Amendments to the claims begin on page 4 of this correspondence.

Remarks begin on page 11

AMENDMENTS TO THE SPECIFICATION

Please amend the specification as follows:

Please replace paragraph 0005 on page 2 of the originally filed specification to read as follows:

--[0005] Applicants have come to appreciate that ~~1,1,1,2,3-~~1,2,3,3,3-pentafluoropropene (HFO-1225ye) and ~~1,1,1,2-~~2,3,3,3-tetrafluoropropene (HFO-1234yf) are each useful in one or more of the above mentioned applications. Accordingly, compositions containing either or both fluorinated olefins are among the materials being developed for such use. --

Please replace paragraph 0008 on page 3 of the originally filed specification to read as follows:

--[0008] Other examples of methods for the production of HFO-1225ye and HFO-1234yf are set forth in, at least, U.S. Pat. No. 7,560,602, which is assigned to the assignee of the present invention and is incorporated herein by reference. This patent discloses a similar dehydrohalogenation process for producing 2,3,3,3-tetrafluoropropene (1234yf) and ~~1,1,1,2,3-~~1,2,3,3,3-pentafluoropropene (HFO-1225ye) by catalytic dehydrofluorination of 1,1,1,2,3-pentafluoropropane (245eb) and 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), respectively. Preferred dehydrohalogenation catalysts include fluorinated chromium oxide catalysts, aluminum fluoride catalysts, ferric fluoride catalysts, mixtures of magnesium fluoride and aluminum fluoride catalysts, nickel-based catalysts, carbon based catalysts, and combinations thereof.--

Please replace paragraph 0021 on page 7 of the originally filed specification to read as follows:

--[0021] In even further embodiments of the foregoing, the second haloolefin is 2,3,3,3-tetrafluoropropene (1234yf) and/or ~~1,1,1,2,3-~~1,2,3,3,3-pentafluoropropene (HFO-1225ye).--

AMENDMENTS TO THE CLAIMS

The following listing of the claims replaces all prior versions and listings:

A Listing of the Claims

1. (Original) A method for producing at least one fluorinated olefin comprising:

   a. hydrogenating a starting material stream comprising at least one alkene according to Formula (I):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_zCX=CH_mX_{2-m} \qquad (I)$$

   by contacting said starting material with a reducing agent to produce an intermediate product stream comprising at least one alkane according to Formula (II):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_zCHXCH_{m+1}X_{2-m} \qquad (II)$$

   where:

   each X is independently Cl, F, I or Br, provided that at least two Xs are F;

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

   each R^1 is independently H, Cl, F, I, Br or unsubstituted or halogen substituted methyl or ethyl radical;

   each R_2 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 0, 1 or 2, provided that a+b = 2;

   m is 0, 1 or 2; and

   z is 0, 1, 2 or 3;

b. optionally, separating said intermediate product stream into a plurality of intermediate product streams, said plurality of intermediate product streams comprising two or more streams selected from the group consisting of a first stream rich in at least a first alkane according to Formula II, a seconds stream rich in at least a second alkane according to Formula II, and an alkane recycle stream;

c. dehydrofluorinating, in the presence of a dehydrohalogenating agent, at least a portion of said intermediate process stream from step (a) or said plurality of intermediate process streams of step (b) to produce an alkene product stream comprising 1,1,1,2,3-pentafluoropropene and at least one additional alkene having a lower degree of fluorine substitution compared to the degree of fluorination of the compound of formula (I); and

d. withdrawing from a dehydrofluorinated product stream a product reaction stream comprising spent dehydrohalogenating agent; and

e. recovering spent dehydrohalogenating agent.

2. (Original) The method of claim 1 wherein said additional alkene is a compound according to formula (III):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_ZCX{=}CH_{m+1}X_{1-m} \text{ (III)}$$

where each of X, Y, R^1, R^2, n, a, and b is the same value as in formula (I) and m is 0 or 1.

3. (Original) The method of claim 2 wherein Z is 0.

4. (Original) The method of claim 3 wherein m is 0 or 1.

5. (Original) The method of claim 4 wherein said n is 3.

6. (Original) The method of claim 5 wherein X is F.

7. (Original) The method of claim 1 wherein said reducing agent is H_2.

8. (Currently amended) The method of claim 1 wherein said starting material stream comprises hexafluoropropylene and said additional alkene is ~~1,1,1,2-~~2,3,3,3-tetrafluoropropene.

9. (Original) The method of claim 1 wherein the dehydrohalogenating agent is selected from the group consisting of KOH, NaOH, $Ca(OH)_2$, LiOH, $Mg(OH)_2$, CaO, and combinations thereof.

10. (Currently amended) A method for producing ~~1,1,1,2-~~2,3,3,3-tetrafluoropropene comprising:

a. hydrogenating a starting material stream comprising hexafluoropropylene by contacting said starting material stream with a reducing agent in a hydrogenation reactor to produce an intermediate stream comprising 1,1,1,2,3-pentafluoropropane or 1,1,1,2,3,3-hexafluoropropane;

b. dehydrofluorinating, in the presence of a dehydrohalogenating agent, said 1,1,1,2,3-pentafluoropropane or said 1,1,1,2,3,3-hexafluoropropane in a dehydrofluorination reactor to produce a product stream comprising ~~1,1,1,2-~~2,3,3,3-tetrafluoropropene or ~~1,1,1,2,3-~~1,2,3,3,3-pentafluoropropene;

c. withdrawing from the product stream a second product stream comprising spent dehydrohalogenating agent; and

d. recovering spent dehydrohalogenating agent.

11. (Original) The process of claim 10 wherein the second product stream further comprises one or more dissolved organics.

12. (Original) The process of claim 11 wherein the dissolved organics are selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,2,3-pentafluoropropane (HFC-245eb), and combinations thereof.

13. (Original) The process of claim 10 wherein the spent dehydrohalogenating agent is purified using at least one separation method.

14. (Original) The process of claim 13 wherein the separation method is selected from the group consisting of distillation or phase separation.

15. (Original) The process of claim 10 further comprising, optionally, concentrating the purified dehydrohalogenating agent and recycling it back to the dehydrohalogenation reaction.

16. (Original) The process of claim 10 wherein the reaction stream further comprises by-product salts of the dehydrohalogenating agent.

17. (Original) The process of claim 16 further comprising converting the by-product salts to the dehydrohalogenating agent.

18. (Original) The process of claim 16 wherein the dehydrohalogenating agent is KOH and the by-product salt is KF.

19. (Original) The process of claim 18 further comprising, optionally, concentrating the converted KOH and recycling it back to the dehydrohalogenation reaction.

20. (Original) The process of claim 18 further comprising converting KF to KOH in the presence of $Ca(OH)_2$.

21. (Original) A process for the manufacture of a fluoroolefin comprising:

(a) dehydrohalogenating a haloalkane in the presence of KOH to produce a haloalkene;

(b) withdrawing a reaction stream comprising spent KOH; and

(c) recovering spent KOH.

22. (Original) The process of claim 21 wherein the haloalkane is comprised of a compound of formula (IIA):

$$(CX_nY_{3-n})CHXCH_{m+1}X_{2-m} \quad (IIA)$$

wherein each X is independently selected from the group consisting of Cl, F, I and Br; each Y is independently selected from the group consisting of H, Cl, F, I, and Br; n is 1,2, or 3; and m is 0, 1 or 2.

23. (Original) The process of claim 22 wherein the haloalkane is 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb).

24. (Original) The process of claim 21 wherein the haloalkene is comprised of a compound of formula (IIIA):

$$(CX_nY_{3-n})CX{=}CH_{m+1}X_{1-m} \quad (IIIA)$$

wherein each X is independently selected from the group consisting of Cl, F, I and Br; each Y is independently selected from the group consisting of H, Cl, F, I, and Br; n is 1,2, or 3; and m is 0 or 1.

25. (Currently amended) The process of claim 24 wherein the haloalkene is 2,3,3,3-~~tetrafluoropropane~~ tetrafluoropropene (HFO-1234yf) or 1,2,3,3,3-pentafluoropropene (HFO-1225ye).

26. (Original) The process of claim 21 wherein the dehydrohalogenation occurs using a continuously stirred tank reactor.

27. (Original) The process of claim 21 wherein the spent KOH is withdrawn from the reactor continuously or intermittently.

28. (Original) The process of claim 21 wherein the reaction stream further comprises a dissolved organics.

29. (Original) The process of claim 28 wherein the dissolved organics are selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb).

30. (Original) The process of claim 21 wherein the spent KOH is purified using at least one separation method.

31. (Original) The process of claim 30 wherein the separation method is selected from the group consisting of distillation or phase separation.

32. (Original) The process of claim 21 further comprising, optionally, concentrating the purified KOH and recycling it back to the dehydrohalogenation reaction.

33. (Original) The process of claim 21 wherein the reaction stream further comprises KF.

34. (Original) The process of claim 3 further comprising converting KF to KOH in the presence of $Ca(OH)_2$.

35. (Original) The process of claim 34 further comprising, optionally, concentrating the converted KOH and recycling it back to the dehydrohalogenation reaction.

36. (Currently amended) A process for the manufacture of a fluoroolefin comprising:

(a) dehydrohalogenating 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb) in the presence of KOH to produce 2,3,3,3-~~tetrafluoropropane~~ tetrafluoropropene (HFO-1234yf) or 1,2,3,3,3-pentafluoropropene (HFO-1225ye);

(b) withdrawing a reaction stream comprising spent KOH; and

(c) recovering spent KOH.

37. (Original) The process of claim 36 wherein the dehydrohalogenation occurs using a continuously stirred tank reactor.

38. (Original) The process of claim 36 wherein the spent KOH is withdrawn from the reactor continuously or intermittently.

39. (Original) The process of claim 36 wherein the reaction stream further comprises a dissolved organics.

40. (Original) The process of claim 37 wherein the dissolved organics are selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb).

41. (Original) The process of claim 36 wherein the spent KOH is purified using at least one separation method.

42. (Original) The process of claim 41 wherein the separation method is selected from the group consisting of distillation or phase separation.

43. (Original) The process of claim 36 further comprising, optionally, concentrating the purified KOH and recycling it back to the dehydrohalogenation reaction.

44. (Original) The process of claim 36 wherein the reaction stream further comprises KF.

45. (Original) The process of claim 44 further comprising purifying KF from the reaction stream.

46. (Original) The process of claim 36 further comprising converting KF to KOH in the presence of $Ca(OH)_2$, optionally, concentrating the KOH and recycling it back to the dehydrohalogenation reaction.

REMARKS

Amendments to the Specification and Claims

Applicants note that the present specification and claims 8 and 10 are amended to provide the correct nomenclature for 1234yf and 1225ye. That it all references to 1,1,1,2-tetrafluoropropene are changed to 2,3,3,3-tetrafluoropropene and all references to 1,1,1,2,3-pentafluoropropene are changed to 1,2,3,3,3-pentafluoropropene. Support for these changes are found throughout the originally filed specification such that no new matter is being added.

Applicants also note that claims 25 and 36 are amended herein correct a typographical error. The term "2,3,3,3-tetrafluoropropane" is corrected to provide "2,3,3,3-tetrafluoropropene." Applicants respectfully assert that no new matter is added by this amendment.

Response to the Restriction Requirement

In the Restriction Requirement dated January 17, 2013, an election of species was requested for each "specific fluoriated olefin, and any specific fluorinated intermediates, and specific starting materials."

Applicants respectfully elect without traverse, as follows:

a. Formula (I): hexafluoropropylene (HFP) – (claims 1-46);

b. Formula (II): 1,1,1,2,3-pentafluoropropane (HFC-245eb) – (claims 1-46);

c. haloalkane of formula (IIA): 1,1,1,2,3-pentafluoropropane (HFC-245eb) – (claims 1-46);

d. additional alkene of formula (III): 2,3,3,3-tetrafluoropropene – (claims 1-46);

e. haloalkene of formula (IIIA): 2,3,3,3-tetrafluoropropene – (claims 1-46);

f. reducing agent: H_2 – (claims 1-46); and

g. dehydrohalogenating agent: KOH – (claims 1-46).

In addition, Applicants respectfully request the search of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) as a second compound of formulas II and IIA and 1,2,3,3,3-pentafluoropropene (HFO-1225ye) as a second compound of formulas III and IIIA. Applicants respectfully assert that such a search would not impose an undue burden on the Office, accordingly examination of the two would be proper.

CONCLUSION

Applicants believe that this reply constitutes a full and complete response to the Restriction Requirement. The Office is invited to contact the undersigned counsel in order to further the prosecution of this application in any way or if further election is believe to be required.

Respectfully submitted,

Dated: February 13, 2013

/J. Eric Sumner/

J. Eric Sumner
Registration No. 58,699
Eagleview Corporate Center
747 Constitution Drive, Suite 100
Exton, PA 19341
Tel: 610-458-6712
Fax: 610-458-7337
Email: esumner@foxrothschild.com

Electronic Acknowledgement Receipt

EFS ID:	14948917
Application Number:	13229016
International Application Number:	
Confirmation Number:	8706
Title of Invention:	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS
First Named Inventor/Applicant Name:	SELMA BEKTESEVIC
Customer Number:	91970
Filer:	John Eric Sumner/Michele Greenberg
Filer Authorized By:	John Eric Sumner
Attorney Docket Number:	H0024680-4511
Receipt Date:	13-FEB-2013
Filing Date:	09-SEP-2011
Time Stamp:	14:25:23
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		int86.PDF	62016 80b03bb2084325d436e9dafcfd76030e77403f2f	yes	12

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Response to Election / Restriction Filed	1	1
	Specification	2	3
	Claims	4	10
	Applicant Arguments/Remarks Made in an Amendment	11	12
Warnings:			
Information:			
	Total Files Size (in bytes):	62016	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

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.

PTO/SB/06 (07-06)
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PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number	Filing Date	☐ To be Mailed
13/229,016	09/09/2011	

APPLICATION AS FILED – PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY ☐ RATE ($)	SMALL ENTITY ☐ FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	OTHER THAN SMALL ENTITY FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =		OR	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =			X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							
			TOTAL			TOTAL	

* If the difference in column 1 is less than zero, enter "0" in column 2.

APPLICATION AS AMENDED – PART II

AMENDMENT 02/13/2013

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE ($)	SMALL ENTITY ADDITIONAL FEE ($)	OR	OTHER THAN SMALL ENTITY RATE ($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	* 46	Minus	** 46	= 0	X $ =		OR	X $62=	0
Independent (37 CFR 1.16(h))	* 4	Minus	***4	= 0	X $ =		OR	X $250=	0
☐ Application Size Fee (37 CFR 1.16(s))									
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	0

AMENDMENT

	(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)		RATE ($)	ADDITIONAL FEE ($)
Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =		OR	X $ =	
Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =		OR	X $ =	
☐ Application Size Fee (37 CFR 1.16(s))									
☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
					TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

Legal Instrument Examiner:
/LINDA BADIE/

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/229,016	09/09/2011	SELMA BEKTESEVIC	H0024680-4511	8706

91970 7590 06/06/2013

HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962

EXAMINER	
BROOKS, CLINTON A	

ART UNIT	PAPER NUMBER
1621	

NOTIFICATION DATE	DELIVERY MODE
06/06/2013	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

patentservices-us@honeywell.com
DL-SM-IP@Honeywell.com

Office Action Summary	Application No. 13/229,016	Applicant(s) BEKTESEVIC ET AL.	
	Examiner CLINTON BROOKS	Art Unit 1621	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *3* MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *13 February 2013*.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

5)☒ Claim(s) *1-46* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☒ Claim(s) *1-10, 21-46* is/are allowed.

7)☒ Claim(s) *11-20* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on *09 September 2011* is/are: a)☒ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some * c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Interim copies:

a)☐ All b)☐ Some c)☐ None of the: Interim copies of the priority documents have been received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date *10/31/2011, 7/31/2012*.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

4) ☐ Other: _____.

DETAILED ACTION

Status of Claims

Claims 1-46 are currently pending.

Priority

The instant application 13/229016, filed 9/9/2011 claims priority as follows:

** CONTINUING DATA **********
This appln claims benefit of 61/392,242 10/12/2010
and is a CIP of 13/195,429 08/01/2011 PAT 8242316
which is a CIP of 12/402,372 03/11/2009 PAT 8013194
which claims benefit of 61/036,526 03/14/2008

Election/Restrictions

In the response received February 13, 2013, Applicant elected without traverse is acknowledged. The election is below.

Applicants respectfully elect without traverse, as follows:

a. Formula (I): hexafluoropropylene (HFP) – (claims 1-46);

b. Formula (II): 1,1,1,2,3-pentafluoropropane (HFC-245eb) – (claims 1-46);

c. haloalkane of formula (IIA): 1,1,1,2,3-pentafluoropropane (HFC-245eb) – (claims 1-46);

d. additional alkene of formula (III): 2,3,3,3-tetrafluoropropene – (claims 1-46);

e. haloalkene of formula (IIIA): 2,3,3,3-tetrafluoropropene – (claims 1-46);

f. reducing agent: H_2 – (claims 1-46); and

g. dehydrohalogenating agent: KOH – (claims 1-46).

Information Disclosure Statement

All references from the IDS(s) statements received 10/31/2011, and 7/31/2012 have been considered unless marked with a strikethrough.

Claim Rejection – 112 Second Paragraph

The following is a quotation of 35 U.S.C. 112(b):

(B) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.

The following is a quotation of 35 U.S.C. 112 (pre-AIA), second paragraph:

The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

Claims 11-20 are rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention.

Claim 11-20 recites the limitation "The process" in the claim. There is insufficient antecedent basis for this limitation in the claim. The claims from which these claims depend recite “A method”. Consistency is required.

Art Made of Record But Not Applied

US-20090234165 (“the ‘165 publication”) discloses a method for producing at least one fluorinated olefin comprising a) a hydrogenation step, b) an optional separation step, and c) a dehydrofluorination step in its claim 1. Further, the '165 publication teaches at [0054] dehydrohalogenating agents. The '165 differs from instant claim 1 in d) withdrawal of the product stream comprising the dehydrohalogenating agent and e) recovery of spent dehydrohalogenating agent. Withdrawal and recovery is not depicted, taught or suggested in D1.

Conclusions

Claims 1-10, 21-46 are allowed.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to CLINTON BROOKS whose telephone number is (571)270-7682. The examiner can normally be reached on Monday-Friday 8:00 AM to 5:00 PM EST.
If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, JOHANN RICHTER can be reached on (571)272-0646. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.
Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/CLINTON BROOKS/

Examiner, Art Unit 1621

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13229016	BEKTESEVIC ET AL.
	Examiner	Art Unit
	CLINTON BROOKS	1621

CPC- SEARCHED		
Symbol	Date	Examiner

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

SEARCH NOTES		
Search Notes	Date	Examiner
Searched EAST (keyword, inventor names, ids; USPAT, USPGPUB, EPO, JPO, DERWEENT)	6/3/2013	/CB/
Searched STN (keyword, inventor names, registry nos; CAPLUS, REGISTRY)	6/3/2013	/CB/
Searched PALM (inventor names)	6/3/2013	/CB/

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner

PTO/SB/08a (01-10)
Approved for use through 07/31/2012. OMB 0651-0031
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	13229016
Filing Date	2011-09-09
First Named Inventor	Selma Bektesevic
Art Unit	1621
Examiner Name	Not Yet Assigned
Attorney Docket Number	H0016235CON-4511

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	5396000		1995-03-07	Nappa et al.	
	2	5679875		1997-10-21	Aoyama et al.	
	3	6031141		2000-02-29	Mallikarjuna et al.	
	4	6548719		2003-04-15	Nair et al.	
	5	5672787		1997-09-30	Bielefeldt et al.	
	6	5714655		1998-02-03	Yamamoto et al.	
	7	4876405		1989-10-24	Gervasutti	
	8	5672803		1997-09-30	Smith et al.	

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.B./

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	13229016 13229016 - GAU: 1621
	Filing Date	2011-09-09
	First Named Inventor	Selma Bektesevic
	Art Unit	1621
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	H0016235CON-4511

	9	6734332		2004-05-11	Slaugh et al.	
	10	7230146		2007-06-12	Merkel et al.	
	11	6369284		2002-04-09	Nappa et al.	
	12	7560602		2009-07-14	Van Der Puy et al.	

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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20070123741		2007-05-31	Van Der Puy et al.	
	2	20060106263		2006-05-18	Miller et al.	
	3	20070129579		2007-06-07	Wang et al.	
	4	20040119047		2004-06-24	Singh et al.	
	5	20110112338		2011-05-12	Smith et al.	

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	First Named Inventor	Selma Bektesevic
	Art Unit	1621
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	H0016235CON-4511

	6	20110021849		2011-01-27	Avril et al.	
	7	20110190554		2011-08-04	Pigamo et al.	
	8	20100305370		2010-12-02	Devic et al.	
	9	20090278075		2009-11-12	Mahler et al.	
	10	20100145111		2010-06-10	Sharratt et al.	
	11	20090234165		2009-09-17	Chiu et al.	
	12	20100029997		2010-02-04	WANG et al.	

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	9833755	WO	A1	1998-08-06	Du Pont et al.		☐
	2	2007/117391	WO	A1	2007-10-18	Du Pont et al.		☐

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	Filing Date	2011-09-09
	First Named Inventor	Selma Bektesevic
	Art Unit	1621
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	H0016235CON-4511

	3	0982281	EP	A1	2000-03-01	Jp Agency Of Ind et al.		☐
	4	0688751	EP	A1	1995-12-27	Bayer Ag	Equivalent to US 5,672,787	☐
	5	0726243	EP	A1	1996-08-14	Daikin Ind Ltd		☐
	6	0442087	EP	A1	1991-08-21	Bayer Ag	Abstract	☐
	7	08165256	JP	A	1996-06-25	Daikin Ind Ltd	Abstract	☐
	8	2152031	CA	A1	1995-12-22	Bayer Ag		☐
	9	0644173	EP	A1	1995-03-22	Daikin Ind Ltd		☐
	10	2011010024	WO	A1	2011-01-27	Arkema France et al.		☐
	11	2935702	FR	A1	2010-03-12	Arkema France		☒
	12	2010139873	WO	A1	2010-12-09	Arkema France et al.		☐
	13	2010029239	WO	A1	2010-03-18	Arkema France et al.		☐

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	Examiner Name	Not Yet Assigned
	Attorney Docket Number	H0016235CON-4511

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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	Meriam-Webster online dictionary, retrieved on 8/26/2009. http://www.merriam-webster.com/dictionary/stage US	☐
	2	KNUNYANTS, ET AL., "Reactions of Fluoro Olefins Communication 13. Catalytic Hydrogenation of Perfluoro Olefins," 1960, Bulletin of the Academy of Sciences of the USSR, Division of Chemical Sciences, pp 1312-1317 (XP000578879) USSR	☐
	3	KIYOSHI ENDO ET AL., "Monomer-Isomerization Polymerization-XXVI. The Case of 2-Butene in the Presence of Isobutene with Ziegler-Natta Catalyst," Eur. Polym. J., Vol. 28, No. 2, pp 153-157 (1992)	☐

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EXAMINER SIGNATURE

Examiner Signature	/Clinton Brooks/	Date Considered	06/03/2013

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	40	US-5396000-$.DID. OR US-5679875-$.DID. OR US-6031141-$.DID. OR US-6548719-$.DID. OR US-5672787-$.DID. OR US-5714655-$.DID. OR US-4876405-$.DID. OR US-5672803-$.DID. OR US-6734332-$.DID. OR US-7230146-$.DID. OR US-6369284-$.DID. OR US-7560602-$.DID. OR US-20070123741-$.DID. OR US-20060106263-$.DID. OR US-20070129579-$.DID. OR US-20040119047-$.DID. OR US-20090278075-$.DID. OR US-20090234165-$.DID. OR US-9833755-$.DID. OR US-2152031-$.DID. OR US-2935702-$.DID.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:19
L2	2	WO-2009084703-$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:20
L3	2	WO-2009125201-$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:20
L5	44	l1 or l2 or l3	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:20
L6	14	bektesevic$selma$.in.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:21
L7	379	tung$hsueh$.in.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:21
L8	24	kopkalli$haluk$.in.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:21

L9	389	l6 or l7 or l8	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:21
L10	0	l9 and hexaflouropropylene	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:22
L11	18	l9 and HFP	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:22
L12	11	l11 and 245eb	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:22
L13	11	l12 and hydrogen	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:22
L14	0	l13 and hydroxie	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:23
L15	4	l13 and hydroxide	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:23
L16	2	"8242316".pn.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:23
L17	1	WO-2012050157-$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:29
L18	1	WO-2012051057-$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:29

L19	1	2012-B24772.NRAN.	DERWENT	OR	ON	2013/06/03 00:29
L20	1	2012-B24772.NRAN.	DERWENT	OR	ON	2013/06/03 00:30
L21	2	US-20090234165-$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:35
L22	17150	"570".clas.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:52
L23	0	halogenating same contacting same separating same dehydrofluorinating	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:53
L24	1	halogenating same contacting same dehydrofluorinating	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:53
L25	4	halogenating and contacting and dehydrofluorinating	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:53
L26	1024	1234yf	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:55
L27	83	l26 and hexafluoropropylene	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:56
L28	66	l27 and (pentafluoropropane or hexafluoropropane)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:56
L29	28	l28 and hydroxide	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 00:57
L30	2	"8013194".pn.	US-PGPUB;	OR	ON	2013/06/03 01:15

			USPAT; USOCR; EPO; JPO; DERWENT			
L31	17150	"570".clas.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:17
L32	2067	l31 and (sodium adj hydroxide)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:18
L33	67059	(sodium adj hydroxide) and recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:18
L34	2068	(sodium adj hydroxide) with recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:18
L35	23	l31 and l34	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:18
L36	2	l35 and dehydrohalogenat$	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:19
L37	59	(sodium adj hydroxide) adj recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:20
L38	0	l37 and "570".clas.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:21
L39	207	hydroxide adj recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:22
L40	2	l39 and "570".clas.	US-PGPUB;	OR	ON	2013/06/03 01:22

			USPAT; USOCR; EPO; JPO; DERWENT			
L41	6	spent with KOH with recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:24
L42	2	spent adj KOH with recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:25
L43	22	spent adj KOH	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/06/03 01:25

EAST Search History (Interference)

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6/ 3/ 2013 1:26:03 AM
C:\ Users\ cbrooks2\ Documents\ EAST\ Workspaces\ 13229016\ 13229016 - keyword - ids-inventor names.wsp

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BIB DATA SHEET

CONFIRMATION NO. 8706

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
13/229,016	09/09/2011	570	1621	H0024680-4511

APPLICANTS

SELMA BEKTESEVIC, Williamsville, NY;
HSUEH SUNG TUNG, Getzville, NY;
HALUK KOPKALLI, Staten Island, NY;

**** CONTINUING DATA ***************************

This appln claims benefit of 61/392,242 10/12/2010
and is a CIP of 13/195,429 08/01/2011 PAT 8242316
which is a CIP of 12/402,372 03/11/2009 PAT 8013194
which claims benefit of 61/036,526 03/14/2008

**** FOREIGN APPLICATIONS ***************************

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED ****

09/20/2011

Foreign Priority claimed	☐ Yes ☑ No		STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS
35 USC 119(a-d) conditions met	☐ Yes ☑ No	☐ Met after Allowance				
Verified and Acknowledged	/CLINTON A BROOKS/ Examiner's Signature	/CB/ Initials	NY	3	46	4

ADDRESS

HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962
UNITED STATES

TITLE

INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS

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2792	FEES: Authority has been given in Paper No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	☐ All Fees ☐ 1.16 Fees (Filing) ☐ 1.17 Fees (Processing Ext. of time) ☐ 1.18 Fees (Issue) ☐ Other _____ ☐ Credit

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	13229016
Filing Date	2011-09-09
First Named Inventor	Selma Bektesevic
Art Unit	1621
Examiner Name	Clinton A. Brooks
Attorney Docket Number	H0024680-4511

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2009/084703	WO	A1	2009-07-09	Daikin Ind Ltd et al.		☐
	2	2009/125201	WO	A2	2009-10-15	Ineos Fluor Holdings Liimited et al.		☐

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	13229016 13229016 - GAU: 1621
	Filing Date	2011-09-09
	First Named Inventor	Selma Bektesevic
	Art Unit	1621
	Examiner Name	Clinton A. Brooks
	Attorney Docket Number	H0024680-4511

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1	PCT/US/2011/55198 Search Report, dated May 4, 2012.	☐

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Examiner Signature	/Clinton Brooks/	Date Considered	06/03/2013

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Filing Date	2011-09-09
First Named Inventor	Selma Bektesevic
Art Unit	1621
Examiner Name	Clinton A. Brooks
Attorney Docket Number	H0024680-4511

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

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OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☒ See attached certification statement.

☐ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☐ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/J. Eric Sumner/	Date (YYYY-MM-DD)	2012-07-31
Name/Print	J. Eric Sumner	Registration Number	58699

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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Docket No.: H0024680-4511
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Selma Bektesevic et al.

Application No.: 13/229,016 Confirmation No.: 8706

Filed: September 9, 2011 Art Unit: 1621

For: Integrated Continuous Process For Dehydrofluorination of 236ea and 245eb Examiner: Clinton A. Brooks

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT (IDS)

MS Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Madam:

In accordance with 37 CFR 1.97, Applicant(s) hereby make of record the following additional documents. A PTO Form SB/08 and a full copy of each of the documents required under 37 CFR 1.98(a)(2) accompany this statement.

Applicant(s) have become aware of the following documents, cited in an International Search Report issued May 4, 2012, during the prosecution of International Application No. PCT/US11/55198, which corresponds to the above referenced application, and in accordance with 37 CFR 1.97(c) and (e)(1) or (b)(3), hereby submit(s) these documents for the Examiner's consideration. These documents are cited on the enclosed PTO Form SB/08, and a copy of the International Search Report and of each document required under 37 CFR 1.98(a)(2) cited thereon are enclosed as well.

This statement is not to be interpreted as a representation that the cited documents are material, that an exhaustive search has been conducted, or that no other relevant information exists. Nor shall the

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citation of any document herein be construed *per se* as a representation that such document is prior art. Moreover, Applicant(s) understand(s) the Examiner will make an independent evaluation of the cited documents.

This Information Disclosure Statement is filed before the mailing date of a first Office Action on the merits as far as is known to the undersigned (37 CFR 1.97(b)(3)).

Furthermore, in accordance with 37 CFR 1.704(d), Applicant(s) note(s) that to our knowledge each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart application and that this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

The Director is hereby authorized to charge any deficiency in the fees filed, asserted to be filed or which should have been filed herewith (or with any paper hereafter filed in this application by this firm) to our Deposit Account No. 50-1943, under Order No. 039643.01561.

Dated: July 31, 2012

Respectfully submitted,

Electronic signature: /J. Eric Sumner/
J. Eric Sumner
Registration No.: 58,699
FOX ROTHSCHILD LLP
2000 Market Street
20th Floor
Philadelphia, Pennsylvania 19103-3222
(215) 299-2772
(215) 299-2150 (Fax)
Attorneys/Agents For Applicant

06/03/2013
/Clinton Brooks/

ALL REFERENCES CONSIDERED EXCEPT WHERE LINED THROUGH. /C.B./

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13229016	BEKTESEVIC ET AL.
	Examiner	Art Unit
	CLINTON BROOKS	1621

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	06/03/2013								
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	2	=								
	3	=								
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	36	=								

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13229016	BEKTESEVIC ET AL.
	Examiner	Art Unit
	CLINTON BROOKS	1621

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	06/03/2013								
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	45	=								
	46	=								

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NEWS	21	JAN 17	Cooperative Patent Classification (CPC) Search and Display Capabilities Now Available in CA/CAplus Family of Databases and USPAT Databases on STN
NEWS	22	JAN 23	INPADOC: CPC Backfile Data Now Available
NEWS	23	JAN 28	Reloaded MEDLINE on STN Now Includes 2013 MeSH Vocabulary and New Fields
NEWS	24	JAN 31	INPADOC Databases Enhanced with Calculated Expiration Dates
NEWS	25	JAN 31	INPADOC Enhanced with Citing Patent Information
NEWS	26	JAN 31	INPAFAMDB Enhanced with Patent Family Counts
NEWS	27	FEB 6	Enhancements to COMPENDEX
NEWS	28	FEB 22	2013 MARPAT Backfile Expansion Update
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NEWS	31	MAR 11	JAPIO Will No Longer Be Updated from March 2013 Onwards
NEWS	32	MAR 22	Cooperative Patent Classification (CPC) Added to USPATOLD

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 NEWS 33  MAR 25  SciSearch on STN Now Includes New Fields
                  Find Grant Information More Easily
 NEWS 34  APR 29  Emtree Thesaurus Updated in Embase
 NEWS 35  APR 29  Embase Alert (EMBAL) Enhanced with Articles-in-Press Content
                  and Optimized for Use as a Companion Database for Embase
 NEWS 36  APR 30  Derwent WPI: The New Cooperative Patent Classification Is
                  Now Available
 NEWS 37  MAY 21  STN Updated to Reflect Streamlining of CAS Roles
 NEWS 38  MAY 24  CABA Has Been Reloaded on May 24, 2013
 NEWS 39  MAY 28  STN Adds Indian Patent Full Text File - INFULL

 NEWS EXPRESS 23 MAY 2012 CURRENT WINDOWS VERSION IS V8.5.1,
              AND CURRENT DISCOVER FILE IS DATED 25 MARCH 2013.

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                                                         ENTRY    SESSION
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FILE LAST UPDATED: 2 Jun 2013 (20130602/ED)
REVISED CLASS FIELDS (/NCL) LAST RELOADED:  May 2013
USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE:  April 2013

CAplus includes complete International Patent Classification (IPC)
reclassification data for the second quarter of 2013.
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CAplus now includes the comprehensive Cooperative Patent Classification (CPC). See HELP CPC for details.

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L1            2 US2012022302/PN
                (US20120022302/PN)

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YOU HAVE REQUESTED DATA FROM 2 ANSWERS - CONTINUE? Y/(N):y

L1   ANSWER 1 OF 2  CAPLUS  COPYRIGHT 2013 ACS on STN
AN   2012:568614  CAPLUS
DN   156:508305
TI   Integrated process for the manufacture of fluorinated olefins
IN   Bektesevic, Selma; Tung, Hsueh Sung; Kopkalli, Haluk
PA   Honeywell International Inc., USA
SO   PCT Int. Appl., 39pp.
     CODEN: PIXXD2
DT   Patent
LA   English
FAN.CNT 3
     PATENT NO.          KIND   DATE        APPLICATION NO.         DATE
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             ZA, ZM, ZW
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     US 2011-229016       A     20110909
     US 2008-36526P       P     20080314
     US 2009-402372       A2    20090311
     US 2011-195429       A2    20110801
ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OS   CASREACT 156:508305

L1   ANSWER 2 OF 2  CAPLUS  COPYRIGHT 2013 ACS on STN
AN   2012:125425  CAPLUS
DN   156:178025
TI   Integrated process for the manufacture of fluorinated olefins
IN   Bektesevic, Selma; Tung, Hsueh Sung; Kopkalli, Haluk
PA   Honeywell International Inc., USA
SO   U.S. Pat. Appl. Publ., 14pp., Cont.-in-part of U.S. Ser. No. 195,429.
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LA   English
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     US 20120301373       A1    20121129    US 2012-570668         20120809
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     US 2011-195429       A2    20110801
     US 2011-229016       A     20110909
ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OS   CASREACT 156:178025; MARPAT 156:178025


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                                                 ENTRY    SESSION
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DICTIONARY FILE UPDATES:  30 MAY 2013  HIGHEST RN 1433279-95-8

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=> d his

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L3   12 L2

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RN   7789-23-3 REGISTRY
ED   Entered STN: 16 Nov 1984
CN   Potassium fluoride (KF) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN   Potassium fluoride (8CI)
OTHER NAMES:
CN   Clocat F
CN   Potassium monofluoride
CN   Potassium monofluoride (KF)
DR   165892-23-9, 59217-74-2
MF   F K
CI   COM
LC   STN Files: ANABSTR, BIOSIS, BIOTECHNO, CA, CAPLUS, CASREACT, CBNB,
       CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN, CSNB, DETHERM*, EMBASE, IFICDB,
       IFIPAT, IFIUDB, MEDLINE, MSDS-OHS, PIRA, RTECS*, TOXCENTER, ULIDAT,
       USPAT2, USPATFULL, USPATOLD
         (*File contains numerically searchable property data)
     Other Sources: DSL**, EINECS**, TSCA**
         (**Enter CHEMLIST File for up-to-date regulatory information)

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           14119 REFERENCES IN FILE CA (1907 TO DATE)
             203 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
           14166 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L3   ANSWER 2 OF 12 REGISTRY COPYRIGHT 2013 ACS on STN
RN   2252-83-7 REGISTRY
ED   Entered STN: 16 Nov 1984
CN   1-Propene, 1,2,3,3,3-pentafluoro- (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN   Propene, 1,2,3,3,3-pentafluoro- (6CI, 7CI, 8CI)

OTHER NAMES:
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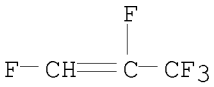
CN 1,1,1,2,3-Pentafluoropropene
CN 1,2,3,3,3-Pentafluoro-1-propene
CN 1,2,3,3,3-Pentafluoropropene
CN 1H-Pentafluoropropene
CN HFC 1225ye
CN HFO 1225ye
CN R 1225Ye
MF C3 H F5
CI COM
SR CA
LC STN Files: CA, CAPLUS, CASREACT, CHEMCATS, CHEMLIST, REAXYSFILE*,
      TOXCENTER, USPAT2, USPATFULL
        (*File contains numerically searchable property data)
    Other Sources: TSCA**
        (**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

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             16 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
            297 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L3 ANSWER 3 OF 12 REGISTRY COPYRIGHT 2013 ACS on STN
RN 1310-73-2 REGISTRY
ED Entered STN: 16 Nov 1984
CN Sodium hydroxide (Na(OH)) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Sodium hydroxide (8CI)
OTHER NAMES:
CN Aetznatron
CN Ascarite
CN Caustic soda
CN Collo-Grillrein
CN Collo-Tapetta
CN DL α
CN DL α
CN E 33
CN E 33 (degreasing agent)
CN FC 4370
CN GR
CN GR (alkali reagent)
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CN NSC 135799
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SR CA
LC STN Files: ADISNEWS, ANABSTR, BIOSIS, BIOTECHNO, CA, CABA, CAPLUS,

CASREACT, CBNB, CHEMCATS, CHEMINFORMRX, CHEMLIST, CHEMSAFE, CIN, CSNB,
DDFU, DETHERM*, DRUGU, EMBASE, ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT,
ENCOMPPAT2, IFICDB, IFIPAT, IFIUDB, IPA, MEDLINE, MSDS-OHS, PATDPASPC,
PIRA, RTECS*, SPECINFO, TOXCENTER, ULIDAT, USAN, USPAT2, USPATFULL, VETU
(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)

Na—OH

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

173972 REFERENCES IN FILE CA (1907 TO DATE)
750 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
175908 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L3 ANSWER 4 OF 12 REGISTRY COPYRIGHT 2013 ACS on STN
RN 1310-65-2 REGISTRY
ED Entered STN: 16 Nov 1984
CN Lithium hydroxide (Li(OH)) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Lithium hydroxide (8CI)
OTHER NAMES:
CN Lithium hydrate
MF H Li O
CI COM
SR CA
LC STN Files: ANABSTR, BIOSIS, BIOTECHNO, CA, CAPLUS, CASREACT, CBNB,
CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN, CSNB, DETHERM*, EMBASE,
ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT, ENCOMPPAT2, IFICDB, IFIPAT, IFIUDB,
MEDLINE, MSDS-OHS, PIRA, RTECS*, TOXCENTER, USAN, USPAT2, USPATFULL,
USPATOLD
(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)

Li—OH

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

16062 REFERENCES IN FILE CA (1907 TO DATE)
130 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
16166 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L3 ANSWER 5 OF 12 REGISTRY COPYRIGHT 2013 ACS on STN
RN 1310-58-3 REGISTRY
ED Entered STN: 16 Nov 1984
CN Potassium hydroxide (K(OH)) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Potassium hydroxide (8CI)
OTHER NAMES:
CN Arrocon 2298
CN Caustic potash
CN Clearcut S
CN Cyantek CC 723
CN Gardoclean S 5167

CN   Potash
CN   PSE 200
DR   71769-53-4, 29857-72-5
MF   H K O
CI   COM
SR   CA
LC   STN Files: ADISNEWS, ANABSTR, BIOSIS, BIOTECHNO, CA, CABA, CAPLUS,
       CASREACT, CBNB, CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN, CSNB, DDFU,
       DETHERM*, DRUGU, EMBASE, ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT, ENCOMPPAT2,
       IFICDB, IFIPAT, IFIUDB, IPA, MEDLINE, MSDS-OHS, PATDPASPC, PIRA, RTECS*,
       TOXCENTER, ULIDAT, USAN, USPAT2, USPATFULL, VETU
         (*File contains numerically searchable property data)
     Other Sources: DSL**, EINECS**, TSCA**
         (**Enter CHEMLIST File for up-to-date regulatory information)

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

           69830 REFERENCES IN FILE CA (1907 TO DATE)
             365 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
           70330 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L3   ANSWER 6 OF 12 REGISTRY COPYRIGHT 2013 ACS on STN
RN   1309-42-8 REGISTRY
ED   Entered STN: 16 Nov 1984
CN   Magnesium hydroxide (Mg(OH)2) (CA INDEX NAME)
OTHER NAMES:
CN   10A
CN   10A (hydroxide)
CN   1110F
CN   200-06H
CN   2M-C01
CN   2N
CN   2N (magnesium hydroxide)
CN   3320HT
CN   5D12
CN   936A
CN   96HS
CN   Alcanex NHC 25
CN   Apymag 40S
CN   Apymag 80S
CN   Apymag AOH 820
CN   Aquamag
CN   Aquamag (hydroxide)
CN   Asahi Glass 200-06
CN   B 54
CN   Burusaito
CN   Combustrol 500
CN   Daimushew 6000
CN   Delamin FRA-B 15
CN   DG 800
CN   DP 393
CN   DSB 100
CN   Duhor
CN   Duhor C 043S
CN   Duhor N
CN   Ebson RF
CN   Echomag PZ 1

CN   Echomag PZ 1G
CN   Echomag PZ 1SP
CN   Echomag ZL
CN   Ecopyrene 5S
CN   Envimag
CN   EP 1
CN   EP 1 (hydroxide)
CN   EP 1A
CN   EPI-A
CN   FD 905U
CN   Finemag MO
CN   Finemag MO-T
CN   Finemag SN-L
CN   FK 621
CN   FloMag H
CN   FloMag HUS
CN   FM 70
CN   FM 70D
CN   FR 20-100D-S7
ADDITIONAL NAMES NOT AVAILABLE IN THIS FORMAT - Use FCN, FIDE, or ALL for DISPLAY
DR   1395893-88-5, 12195-86-7, 13760-51-5
MF   H2 Mg O2
CI   COM
SR   CA
LC   STN Files: ADISNEWS, ANABSTR, BIOSIS, BIOTECHNO, CA, CAPLUS, CASREACT, CBNB, CHEMCATS, CHEMLIST, CIN, CSNB, DDFU, DETHERM*, DRUGU, EMBASE, ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT, ENCOMPPAT2, IFICDB, IFIPAT, IFIUDB, IPA, MEDLINE, MSDS-OHS, PIRA, RTECS*, TOXCENTER, USAN, USPAT2, USPATFULL, USPATOLD, VETU
(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)

HO—Mg—OH

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

25748 REFERENCES IN FILE CA (1907 TO DATE)
293 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
25864 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L3   ANSWER 7 OF 12 REGISTRY COPYRIGHT 2013 ACS on STN
RN   1305-78-8 REGISTRY
ED   Entered STN: 16 Nov 1984
CN   Calcium oxide (CaO) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN   Calcium oxide (6CI, 8CI)
OTHER NAMES:
CN   Airlock
CN   Bell CML 41
CN   Bell CML(E)
CN   Bell CML(P)
CN   Borumikku
CN   Burnt lime
CN   CA 602
CN   CAC 20209A
CN   Calcia
CN   Calcia (CaO)

CN Calciogreen
CN Calcium monoxide
CN Caloxal CPA
CN Caloxol CP 2
CN Caloxol W 3
CN Caltrac
CN Calx
CN Calxyl
CN Chelan
CN CML 21
CN CML 31
CN CML 35
CN CML 35S
CN CSQ
CN Desical P
CN DryPaste S 1
CN E 529
CN F Raimu 1300D
CN F Raimu 900K
CN FCA 8A
CN Fishcal
CN KSX
CN Mikuronraimu
CN Moisutoppu 10
CN Moisutoppu 20
CN NanoActive Calcium Oxide
CN NanoActive CaO
CN NanoActive CaO Plus
CN Nanotek CaO
CN OM 1
CN OM 1 (pigment)
CN Polycal OFT 15
CN Power-Ca
CN QC-X
CN Quicklime (CaO)
CN Rhenofit C
CN Rhenofit F
CN Rhenogran CaO 80
CN Rhenosorb C
ADDITIONAL NAMES NOT AVAILABLE IN THIS FORMAT - Use FCN, FIDE, or ALL for DISPLAY
DR 12610-14-9, 104624-96-6, 60873-85-0, 245321-52-2
MF Ca O
CI COM
SR CA
LC STN Files: ANABSTR, BIOSIS, BIOTECHNO, CA, CABA, CAPLUS, CASREACT, CBNB, CHEMCATS, CHEMINFORMRX, CHEMLIST, CHEMSAFE, CIN, CSNB, DETHERM*, EMBASE, ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT, ENCOMPPAT2, IFICDB, IFIPAT, IFIUDB, IPA, MEDLINE, MSDS-OHS, PIRA, RTECS*, TOXCENTER, ULIDAT, USAN, USPAT2, USPATFULL, VETU
(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)

Ca=O

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

93236 REFERENCES IN FILE CA (1907 TO DATE)

737 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
93970 REFERENCES IN FILE CAPLUS (1907 TO DATE)

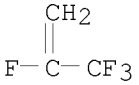
L3 ANSWER 8 OF 12 REGISTRY COPYRIGHT 2013 ACS on STN
RN 1305-62-0 REGISTRY
ED Entered STN: 16 Nov 1984
CN Calcium hydroxide (Ca(OH)2) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Calcium hydroxide (8CI)
OTHER NAMES:
CN A-Rock
CN Biocalc
CN BTTE
CN Cal-Z
CN Calbit
CN Calbreed
CN Calcicure
CN Calcium dihydroxide
CN Calcium Hydroxide Plus Points
CN Caldic 1000
CN Caldic 2000
CN Calen
CN Calvit
CN Carboxide
CN CH 2N
CN CLS-B
CN Ecolomaster
CN HA 20
CN HA 20 (hydroxide)
CN High Purity Calcium Hydroxide CH
CN HP-XL
CN Hydralime
CN Hydrated lime
CN JIS-R 9001
CN Kalic
CN Kalkhydrate
CN Karutekku LT
CN Kentoku K 100
CN Limbux
CN Lime hydrate
CN Lime milk
CN Lime S
CN Lime Type S
CN Lime water
CN LoFloSorb
CN Microstar T
CN Milk of lime
CN Nekablanc 0
CN Nekapur 2
CN NICC 3000
CN NICC 5000
CN Omix C
CN Precal 54
CN Rhein CF 1
CN Rhenofit CF
CN SA 074
CN SA 149
CN Slaked lime
CN Soprocal
ADDITIONAL NAMES NOT AVAILABLE IN THIS FORMAT - Use FCN, FIDE, or ALL for DISPLAY
DR 7719-01-9, 1333-29-5

MF Ca H2 O2
CI COM
SR CA
LC STN Files: ADISNEWS, ANABSTR, BIOSIS, BIOTECHNO, CA, CABA, CAPLUS,
    CASREACT, CBNB, CHEMCATS, CHEMINFORMRX, CHEMLIST, CHEMSAFE, CIN, CSNB,
    DDFU, DETHERM*, DRUGU, EMBASE, ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT,
    ENCOMPPAT2, IFICDB, IFIPAT, IFIUDB, IPA, MEDLINE, MSDS-OHS, PIRA,
    RTECS*, TOXCENTER, USAN, USPAT2, USPATFULL, USPATOLD, VETU
      (*File contains numerically searchable property data)
    Other Sources: DSL**, EINECS**, TSCA**
      (**Enter CHEMLIST File for up-to-date regulatory information)

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

        46292 REFERENCES IN FILE CA (1907 TO DATE)
          385 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
        46519 REFERENCES IN FILE CAPLUS (1907 TO DATE)

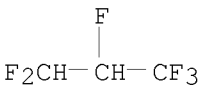
L3 ANSWER 9 OF 12 REGISTRY COPYRIGHT 2013 ACS on STN
RN 754-12-1 REGISTRY
ED Entered STN: 16 Nov 1984
CN 1-Propene, 2,3,3,3-tetrafluoro- (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Propene, 2,3,3,3-tetrafluoro- (6CI, 7CI, 8CI)
OTHER NAMES:
CN 1,1,1,2-Tetrafluoro-2-propene
CN 1,1,1,2-Tetrafluoropropene
CN 1234yf
CN 2,3,3,3-Tetrafluoro-1-propene
CN 2,3,3,3-Tetrafluoropropene
CN 2,3,3,3-Tetrafluoropropylene
CN HFC 1134yf
CN HFC 1234yf
CN HFO 1234yf
CN R 1234yf
MF C3 H2 F4
CI COM
SR CA
LC STN Files: CA, CAPLUS, CASREACT, CBNB, CHEMCATS, CHEMINFORMRX, CHEMLIST,
    CIN, REAXYSFILE*, RTECS*, TOXCENTER, ULIDAT, USPAT2, USPATFULL, USPATOLD
      (*File contains numerically searchable property data)
    Other Sources: TSCA**
      (**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

          894 REFERENCES IN FILE CA (1907 TO DATE)
           22 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
          909 REFERENCES IN FILE CAPLUS (1907 TO DATE)

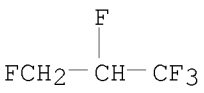
L3 ANSWER 10 OF 12 REGISTRY COPYRIGHT 2013 ACS on STN
RN 431-63-0 REGISTRY
ED Entered STN: 16 Nov 1984
CN Propane, 1,1,1,2,3,3-hexafluoro- (CA INDEX NAME)
OTHER NAMES:
CN 1,1,1,2,3,3-Hexafluoropropane
CN 1,1,2,3,3,3-Hexafluoropropane
CN F 236ea
CN HFC 236ea
CN R 236ea
MF C3 H2 F6
CI COM
SR CA
LC STN Files: CA, CAPLUS, CASREACT, CHEMCATS, CHEMLIST, DETHERM*, MSDS-OHS,
      REAXYSFILE*, RTECS*, TOXCENTER, USPAT2, USPATFULL
        (*File contains numerically searchable property data)
    Other Sources: EINECS**, TSCA**
        (**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

            511 REFERENCES IN FILE CA (1907 TO DATE)
              1 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
            517 REFERENCES IN FILE CAPLUS (1907 TO DATE)

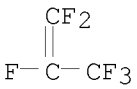
L3 ANSWER 11 OF 12 REGISTRY COPYRIGHT 2013 ACS on STN
RN 431-31-2 REGISTRY
ED Entered STN: 16 Nov 1984
CN Propane, 1,1,1,2,3-pentafluoro- (CA INDEX NAME)
OTHER NAMES:
CN 1,1,1,2,3-Pentafluoropropane
CN 1,2,3,3,3-Pentafluoropropane
CN HFC 245eb
CN R 245eb
MF C3 H3 F5
CI COM
SR CA
LC STN Files: CA, CAPLUS, CASREACT, CHEMCATS, CHEMLIST, REAXYSFILE*,
      TOXCENTER, USPAT2, USPATFULL
        (*File contains numerically searchable property data)
    Other Sources: TSCA**
        (**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

            239 REFERENCES IN FILE CA (1907 TO DATE)
              3 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
            239 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L3 ANSWER 12 OF 12 REGISTRY COPYRIGHT 2013 ACS on STN
RN 116-15-4 REGISTRY
ED Entered STN: 16 Nov 1984
CN 1-Propene, 1,1,2,3,3,3-hexafluoro- (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Propene, hexafluoro- (8CI)
OTHER NAMES:
CN 1,1,2,3,3,3-Hexafluoro-1-propene
CN 1,1,2,3,3,3-Hexafluoropropene
CN Esafluoropropene
CN F 1216
CN Hexafluoro-1-propene
CN Hexafluoropropene
CN Hexafluoropropylene
CN HFC 1216
CN Perfluoro-1-propene
CN Perfluoropropene
CN Perfluoropropylene
CN PFC 1216
CN Propylene hexafluoride
CN R 1216
MF C3 F6
CI COM
SR CA
LC STN Files: ANABSTR, BIOSIS, CA, CAPLUS, CASREACT, CBNB, CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN, CSNB, DETHERM*, EMBASE, ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT, ENCOMPPAT2, IFICDB, IFIPAT, IFIUDB, MEDLINE, MSDS-OHS, PIRA, REAXYSFILE*, RTECS*, SPECINFO, TOXCENTER, ULIDAT, USPAT2, USPATFULL, USPATOLD
(*File contains numerically searchable property data)
Other Sources: EINECS**, NDSL**, TSCA**
(**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

3810 REFERENCES IN FILE CA (1907 TO DATE)
807 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
3816 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> file caplus

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	30.18	73.32

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FILE LAST UPDATED: 2 Jun 2013 (20130602/ED)
REVISED CLASS FIELDS (/NCL) LAST RELOADED: May 2013
USPTO MANUAL OF CLASSIFICATIONS THESAURUS ISSUE DATE: April 2013

CAplus includes complete International Patent Classification (IPC)
reclassification data for the second quarter of 2013.

CAplus now includes the comprehensive Cooperative Patent Classification
(CPC). See HELP CPC for details.

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http://www.cas.org/legal/infopolicy

This file contains CAS Registry Numbers for easy and accurate
substance identification.

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=> s dehydrofluorinate
            10 DEHYDROFLUORINATE
             3 DEHYDROFLUORINATES
L4          13 DEHYDROFLUORINATE
                (DEHYDROFLUORINATE OR DEHYDROFLUORINATES)

=> s l4 and recovery
        639647 RECOVERY
         68461 RECOVERIES
        696372 RECOVERY
                (RECOVERY OR RECOVERIES)
L5           0 L4 AND RECOVERY

=> s bektesevic selma/au
L6          22 BEKTESEVIC SELMA/AU

=> s tung hsueh/au
L7           0 TUNG HSUEH/AU

=> e tung hsueh/au
E1           1     TUNG HSUANG SHENG/AU
E2           3     TUNG HSUCH SUNG/AU
E3           0 --> TUNG HSUEH/AU
E4           3     TUNG HSUEH LI/AU
E5          46     TUNG HSUEH S/AU
E6         136     TUNG HSUEH SUNG/AU
E7           2     TUNG HSUEH SUNG HARRY/AU
E8          23     TUNG HSUEHSUNG/AU
E9           1     TUNG HSUIU CHI/AU
E10          1     TUNG HU SU/AU
E11          2     TUNG HUA SU/AU
E12          1     TUNG HUAN/AU

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             0 "TUNG HSUEH"/AU
             3 "TUNG HSUEH LI"/AU
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           136 "TUNG HSUEH SUNG"/AU
             2 "TUNG HSUEH SUNG HARRY"/AU
L8         187 ("TUNG HSUEH"/AU OR "TUNG HSUEH LI"/AU OR "TUNG HSUEH S"/AU OR
               "TUNG HSUEH SUNG"/AU OR "TUNG HSUEH SUNG HARRY"/AU)

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E2           1     KOPKAB MARY L/AU
E3          23 --> KOPKALLI HALUK/AU
E4           4     KOPKALLI YASEMIN/AU
E5           2     KOPKAN L/AU
E6          23     KOPKAN LIBOR/AU
E7           1     KOPKANE DANIEL/AU
E8           1     KOPKAR SHRIPAD M/AU
E9           4     KOPKE/AU
E10          2     KOPKE A K E/AU
E11          3     KOPKE ADOLF/AU
E12          1     KOPKE AGUIAR L A/AU

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L9          23 "KOPKALLI HALUK"/AU

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        945891 RECOVER?
L11         20 L10 AND RECOVER?

=> d l11 abs ibib hitstr 1-
YOU HAVE REQUESTED DATA FROM 20 ANSWERS - CONTINUE? Y/(N):y

L11  ANSWER 1 OF 20  CAPLUS  COPYRIGHT 2013 ACS on STN
AB   Disclosed is a process for the manufacture of haloalkane compds., and more
     particularly, an improved process for the manufacture of the compound
     1,1,1,3,3-pentachloropropane (HCC-240fa), which mitigates the formation of
     byproducts from vinyl chloride (CH2:CHCl).  The present invention is also
     useful in the manufacture of other haloalkane compds. such as HCC-250 and
     HCC-360.  One embodiment of the invention comprises a method for
     mitigating 1,1,3,3,5,5-hexachloropentane and 1,1,1,3,5,5-hexachloropentane
     formation in the HCC-240fa manufacturing process, in which FeCl3, is introduced
     to a reactor only after the start-up phase has ended and a continuous
     operation has started.  In a preferred embodiment, "pre-chelated" FeCl3,
     which is concentrated in a catalyst recovery column, is introduced to reactor
     after the continuous operation has started.
ACCESSION NUMBER:        2012:1782102  CAPLUS
DOCUMENT NUMBER:         157:737530
TITLE:                   Method for mitigating the formation of by-products
                         during the production of haloalkane compounds
INVENTOR(S):             Close, Joshua; Wang, Haiyou; Tung, Hsueh Sung
PATENT ASSIGNEE(S):      Honeywell International Inc., USA
SOURCE:                  U.S. Pat. Appl. Publ., 6pp.; Chemical Indexing
                         Equivalent to 157:737523 (WO)
                         CODEN: USXXCO
DOCUMENT TYPE:           Patent
LANGUAGE:                English
FAMILY ACC. NUM. COUNT:  2
PATENT INFORMATION:

     PATENT NO.          KIND   DATE        APPLICATION NO.        DATE
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US 20120310021 A1 20121206 US 2012-481121 20120525
WO 2012166759 A2 20121206 WO 2012-US39922 20120530
WO 2012166759 A3 20130307
W: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW
RW: AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, RU, TJ, TM
PRIORITY APPLN. INFO.: US 2011-492898P P 20110603
US 2011-492931P P 20110603
US 2012-481121 A 20120525
ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT

L11 ANSWER 2 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB Disclosed is a process for the manufacture of haloalkane compds., and more particularly, an improved process for the manufacture of the compound 1,1,1,3,3-pentachloropropane (HCC-240fa), which mitigates the formation of byproducts from vinyl chloride (CH2:CHCl). The present invention is also useful in the manufacture of other haloalkane compds. such as HCC-250 and HCC-360. One embodiment of the invention comprises a method for mitigating 1,1,3,3,5,5-hexachloropentane and 1,1,1,3,5,5-hexachloropentane formation in the HCC-240fa manufacturing process, in which FeCl3, is introduced to a reactor only after the start-up phase has ended and a continuous operation has started. In a preferred embodiment, "pre-chelated" FeCl3, which is concentrated in a catalyst recovery column, is introduced to reactor after the continuous operation has started.
ACCESSION NUMBER: 2012:1774012 CAPLUS
DOCUMENT NUMBER: 157:737523
TITLE: Method for mitigating the formation of by-products during the production of haloalkane compounds
INVENTOR(S): Close, Joshua; Wang, Haiyou; Tung, Hsueh Sung
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: PCT Int. Appl., 17pp.; Chemical Indexing Equivalent to 157:737530 (US)
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2012166759	A2	20121206	WO 2012-US39922	20120530
WO 2012166759	A3	20130307		

W: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW
RW: AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS,

SE, SI, SK, SM, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,
MR, NE, SN, TD, TG, BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD,
SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, RU, TJ, TM

US 20120310021	A1	20121206	US 2012-481121	20120525
PRIORITY APPLN. INFO.:			US 2011-492898P P	20110603
			US 2011-492931P P	20110603
			US 2012-481121 A	20120525

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT

L11 ANSWER 3 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN

AB The invention relates to a continuous, integrated manufacturing process for the production of trans-1-chloro-3,3,3-trifluoropropene which comprises: (a) dehydrochlorinating 1,1,1-trifluoro-3,3-dichloropropane (HCFC-243fa) to thereby produce a product stream comprising cis-1-chloro-3,3,3-trifluoropropene, trans-1-chloro-3,3,3-trifluoropropene, and hydrogen chloride; (b) optionally recovering the hydrogen chloride from the product stream of step (a); (c) isomerizing at least a portion of the cis-1-chloro-3,3,3-trifluoropropene into trans-1-chloro-3,3,3-trifluoropropene; and (d) separating and purifying trans-1-chloro-3,3,3-trifluoropropene product.

ACCESSION NUMBER: 2012:1561343 CAPLUS
DOCUMENT NUMBER: 157:608382
TITLE: Process for manufacturing trans-1-chloro-3,3,3-trifluoropropene by catalytic dehydrochlorination of 1,1,1-trifluoro-3,3-dichloropropane
INVENTOR(S): Wang, Haiyou; Tung, Hsueh Sung
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: PCT Int. Appl., 15pp.; Chemical Indexing Equivalent to 157:608368 (US)
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2012145188	A2	20121026	WO 2012-US32830	20120410
WO 2012145188	A3	20130103		

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RW: AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

US 20120271069	A1	20121025	US 2011-90477	20110420
PRIORITY APPLN. INFO.:			US 2011-90477 A	20110420

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): CASREACT 157:608382

L11 ANSWER 4 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN

AB The invention relates to a continuous, integrated manufacturing process for the production of trans-1-chloro-3,3,3-trifluoropropene which comprises: (a)

dehydrochlorinating 1,1,1-trifluoro-3,3-dichloropropane (HCFC-243fa) to thereby produce a product stream comprising cis-1-chloro-3,3,3-trifluoropropene, trans-1-chloro-3,3,3-trifluoropropene, and hydrogen chloride; (b) optionally recovering the hydrogen chloride from the product stream of step (a); (c) isomerizing at least a portion of the cis-1-chloro-3,3,3-trifluoropropene into trans-1-chloro-3,3,3-trifluoropropene; and (d) separating and purifying trans-1-chloro-3,3,3-trifluoropropene product.

ACCESSION NUMBER: 2012:1558268 CAPLUS
DOCUMENT NUMBER: 157:608368
TITLE: Process for manufacturing trans-1-chloro-3,3,3-trifluoropropene by catalytic dehydrochlorination of 1,1,1-trifluoro-3,3-dichloropropane
INVENTOR(S): Wang, Haiyou; Tung, Hsueh Sung
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: U.S. Pat. Appl. Publ., 5pp.; Chemical Indexing Equivalent to 157:608382 (WO)
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 20120271069	A1	20121025	US 2011-90477	20110420
WO 2012145188	A2	20121026	WO 2012-US32830	20120410
WO 2012145188	A3	20130103		

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PRIORITY APPLN. INFO.: US 2011-90477 A 20110420
ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): CASREACT 157:608368

L11 ANSWER 5 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB The instant invention relates, at least in part, to a method increasing the cost efficiency for dehydrohalogenation production of a fluorinated olefin by recovering and recycling spent dehydrohalogenation agent. In one aspect, the present invention relates to dehydrohalogenating a fluorinated alkane (e.g. pentafluoropropane and/or hexafluoropropane) in the presence of a dehydrohalogenating agent to produce a fluorinated olefin (e.g. tetrafluoropropenes and/or pentafluoropropenes). Removal of spent dehydrohalogenating agent from the reactor allows for facile separation of organic and dehydrohalogenating agent, the latter of which is recycled.

ACCESSION NUMBER: 2012:568614 CAPLUS
DOCUMENT NUMBER: 156:508305
TITLE: Integrated process for the manufacture of fluorinated olefins

INVENTOR(S): Bektesevic, Selma; Tung, Hsueh Sung; Kopkalli, Haluk
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: PCT Int. Appl., 39pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 3
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2012051057	A2	20120419	WO 2011-US55198	20111007
WO 2012051057	A3	20120621		
W: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW				
RW: AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
US 20120022302	A1	20120126	US 2011-229016	20110909

PRIORITY APPLN. INFO.:

US 2010-392242P	P	20101012
US 2011-229016	A	20110909
US 2008-36526P	P	20080314
US 2009-402372	A2	20090311
US 2011-195429	A2	20110801

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): CASREACT 156:508305

L11 ANSWER 6 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB An integrated manufacturing process to co-produce (E)-1-chloro-3,3,3-trifluoropropene, (E)-1,3,3,3-tetrafluoropropene, and 1,1,1,3,3-pentafluoropropane starting from a single chlorinated hydrocarbon feed stock, HCC 240fa is described. The process includes a combined liquid or vapor phase reaction/purification operation which directly produces (E)-1-chloro-3,3,3-trifluoropropene (1233zd(E)) from 240fa. In the second liquid phase fluorination reactor 1233zd(E) is contacted with HF in the presence of catalyst to produce 1,1,1,3,3-pentafluoropropane (245fa) with high conversion and selectivity. A third reactor is used for dehydrofluorination of 245fa to produce (E)-1,3,3,3-tetrafluoropropene (1234ze(E)) by contacting in the liquid phase with a caustic solution or in the vapor phase using a dehydrofluorination catalyst. This operation may be followed by ≥1 purification processes to recover the HFC 1234ze(E) product.
ACCESSION NUMBER: 2012:345836 CAPLUS
DOCUMENT NUMBER: 156:339387
TITLE: Integrated process to coproduce trans-1-chloro-3,3,3-trifluoropropene, trans-1,3,3,3-tetrafluoropropene, and 1,1,1,3,3-pentafluoropropane
INVENTOR(S): Pokrovski, Konstantin A.; Merkel, Daniel C.; Wang, Haiyou; Tung, Hsueh Sung; Shankland, Ian
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: U.S. Pat. Appl. Publ., 11pp.
CODEN: USXXCO
DOCUMENT TYPE: Patent

LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 20120059200	A1	20120308	US 2011-219831	20110829
WO 2012030781	A2	20120308	WO 2011-US49665	20110830
WO 2012030781	A3	20120705		

W: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW

RW: AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

PRIORITY APPLN. INFO.: US 2010-379745P P 20100903
US 2011-219831 A 20110829
ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT

L11 ANSWER 7 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB The instant invention relates, at least in part, to a method increasing the cost efficiency for dehydrohalogenation production of a fluorinated olefin by recovering and recycling spent dehydrohalogenation agent. In one aspect, the present invention relates to dehydrohalogenating a fluorinated alkane (e.g. pentafluoropropane and/or hexafluoropropane) in the presence of a dehydrohalogenating agent to produce a fluorinated olefin (e.g. tetrafluoropropenes and/or pentafluoropropenes). Removal of spent dehydrohalogenating agent from the reactor allows for facile separation of organic and dehydrohalogenating agent, the latter of which is recycled.
ACCESSION NUMBER: 2012:125425 CAPLUS
DOCUMENT NUMBER: 156:178025
TITLE: Integrated process for the manufacture of fluorinated olefins
INVENTOR(S): Bektesevic, Selma; Tung, Hsueh Sung; Kopkalli, Haluk
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: U.S. Pat. Appl. Publ., 14pp., Cont.-in-part of U.S. Ser. No. 195,429.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 3
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 20120022302	A1	20120126	US 2011-229016	20110909
US 20090234165	A1	20090917	US 2009-402372	20090311
US 8013194	B2	20110906		
IN 2009DE00492	A	20090918	IN 2009-DE492	20090313
ES 2355541	T3	20110328	ES 2009-155177	20090313
US 20110288347	A1	20111124	US 2011-195429	20110801
US 8242316	B2	20120814		
WO 2012051057	A2	20120419	WO 2011-US55198	20111007
WO 2012051057	A3	20120621		

W: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW

RW: AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

US 20120301373 A1 20121129 US 2012-570668 20120809

PRIORITY APPLN. INFO.: US 2008-36526P P 20080314
US 2009-402372 A2 20090311
US 2010-392242P P 20101012
US 2011-195429 A2 20110801
US 2011-229016 A 20110909

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT

OTHER SOURCE(S): CASREACT 156:178025; MARPAT 156:178025

L11 ANSWER 8 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN

AB The invention presents a method for preparing 2,3,3,3-tetrafluoroprop-1-ene where method involves (a) providing a starting composition comprising at least one compound from CX2=CCl-CH2X, CX3-CCl=CH2,CX3-CHCl-CH2X where X is independently selected from F, Cl, Br, and I, provided that at least one X is not fluorine, (b) contacting the starting composition with a first fluorinating agent to produce a first intermediate composition comprising 2-chloro-3,3,3-trifluoropropene and a first chlorine-containing byproduct, (c) contacting the first intermediate composition with a second fluorinating agent to produce a second intermediate composition comprising 2-chloro-1,1,1,2-tetrafluoropropane and a second chlorine-containing byproduct, and (d) catalytically dehydrochlorinating at least a portion of said 2-chloro-1,1,1,2-tetrafluoropropane to produce a reaction product comprising 2,3,3,3-tetrafluoroprop-1-ene.

ACCESSION NUMBER: 2011:1464811 CAPLUS

DOCUMENT NUMBER: 155:615800

TITLE: Integrated process for production of 2,3,3,3-tetrafluoropropene from halogenated propanes/propenes by fluorination and dehydrochlorination

INVENTOR(S): Merkel, Daniel C.; Tung, Hsueh Sung; Pokrovski, Konstantin A.; Bektesevic, Selma; Johnson, Robert C.; Wang, Haiyou

PATENT ASSIGNEE(S): Honeywell International Inc., USA

SOURCE: U.S., 18pp., Cont.-in-part of U.S. Ser. No. 619,592. CODEN: USXXAM

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 74

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 8058486	B2	20111115	US 2009-404130	20090313
US 20090240090	A1	20090924		
US 20110207975	A9	20110825		
US 20050245773	A1	20051103	US 2005-118503	20050429
US 7345209	B2	20080318		
US 20050245774	A1	20051103	US 2005-118504	20050429
US 7371904	B2	20080513		

CA 2564897 A1 20051117 CA 2005-2564897 20050429
CA 2564897 C 20121127
CA 2564903 A1 20051117 CA 2005-2564903 20050429
CA 2564903 C 20121204
US 20060030744 A1 20060209 US 2005-118530 20050429
US 7189884 B2 20070313
EP 1740518 A1 20070110 EP 2005-740929 20050429
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR
EP 1740521 A1 20070110 EP 2005-744032 20050429
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CN 1968915 A 20070523 CN 2005-80020225 20050429
CN 1968915 B 20110803
CN 1972887 A 20070530 CN 2005-80020412 20050429
CN 1972887 B 20101013
JP 2007535561 T 20071206 JP 2007-511040 20050429
JP 4864878 B2 20120201
JP 2007535570 T 20071206 JP 2007-511080 20050429
JP 4864879 B2 20120201
MX 2006012467 A 20070129 MX 2006-12467 20061027
MX 2006012468 A 20070129 MX 2006-12468 20061027
KR 2007005737 A 20070110 KR 2006-7025179 20061129
KR 2007011554 A 20070124 KR 2006-7025180 20061129
US 20070197842 A1 20070823 US 2007-619592 20070103
US 8084653 B2 20111227
EP 2543655 A2 20130109 EP 2012-178203 20070103
EP 2543655 A3 20130508
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR
EP 2546220 A2 20130116 EP 2012-178195 20070103
EP 2546220 A3 20130508
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR
EP 2546221 A2 20130116 EP 2012-178198 20070103
EP 2546221 A3 20130508
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR
EP 2546222 A2 20130116 EP 2012-178204 20070103
EP 2546222 A3 20130508
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR
EP 2546223 A2 20130116 EP 2012-178207 20070103
EP 2546223 A3 20130508
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR
EP 2546224 A2 20130116 EP 2012-178208 20070103
EP 2546224 A3 20130508
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EP 2546225 A2 20130116 EP 2012-178209 20070103
EP 2546225 A3 20130508
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR
CA 2608327 A1 20080427 CA 2007-2608327 20071026
CA 2608675 A1 20080427 CA 2007-2608675 20071026
EP 1916231 A2 20080430 EP 2007-119432 20071026
EP 1916231 A3 20091223
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR, AL, BA, HR, MK, RS
EP 1916232 A1 20080430 EP 2007-119443 20071026

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            AL, BA, HR, MK, RS
    MX 2007013508        A     20081028    MX 2007-13508          20071026
    MX 2007013510        A     20081028    MX 2007-13510          20071026
    EP 2338866           A1    20110629    EP 2011-841            20071026
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    KR 2008038074        A     20080502    KR 2007-109198         20071029
    KR 2008038075        A     20080502    KR 2007-109199         20071029
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    CN 101182280         A     20080521    CN 2007-10199937       20071029
    CN 101182280         B     20120627
    JP 2008162999        A     20080717    JP 2007-280719         20071029
    CN 101260021         A     20080910    CN 2007-10159615       20071029
    EP 2103587           A2    20090923    EP 2009-155292         20090316
    EP 2103587           A3    20100303
    EP 2103587           B1    20130220
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    MX 2009002967        A     20090928    MX 2009-2967           20090319
    JP 2009227675        A     20091008    JP 2009-67988          20090319
    CN 101597209         A     20091209    CN 2009-10138775       20090319
    KR 2009101128        A     20090924    KR 2009-24122          20090320
    IN 2009DE00535       A     20091002    IN 2009-DE535          20090320
    WO 2011068649        A2    20110609    WO 2010-US56291        20101111
    WO 2011068649        A3    20111013
        W:  AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,
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            ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP,
            KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA,
            MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE,
            PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV,
            SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW
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            HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS,
            SE, SI, SK, SM, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,
            MR, NE, SN, TD, TG, BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL,
            SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
    AU 2011202712        A1    20110630    AU 2011-202712         20110607
    AU 2011202712        B2    20120119
    AU 2011202712        B9    20120308
    JP 2011236226        A     20111124    JP 2011-142048         20110627
    JP 2011236227        A     20111124    JP 2011-142053         20110627
    JP 2011236228        A     20111124    JP 2011-142058         20110627
    AU 2011213796        A1    20110922    AU 2011-213796         20110819
    AU 2011213796        B2    20120927
    AU 2012202305        A1    20120510    AU 2012-202305         20120419
    AU 2012202525        A1    20120524    AU 2012-202525         20120501
    AU 2012265607        A1    20130110    AU 2012-265607         20121219
    AU 2013203977        A1    20130509    AU 2013-203977         20130411
PRIORITY APPLN. INFO.:                      US 2004-567425P     P  20040429
                                            US 2004-567426P     P  20040429
                                            US 2004-567427P     P  20040429
                                            US 2004-567428P     P  20040429
                                            US 2004-567429P     P  20040429
                                            US 2005-118503      A2 20050429
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US 2005-118504	A2	20050429
US 2005-118530	A2	20050429
US 2006-755485P	P	20060103
US 2007-619592	A2	20070103
US 2008-38327P	P	20080320
JP 2007-511040	A3	20050429
JP 2007-511080	A3	20050429
JP 2007-511081	A3	20050429
WO 2005-US14950	W	20050429
WO 2005-US15124	W	20050429
AU 2006-261816		20060626
US 2006-588465	A	20061027
US 2006-588671	A	20061027
EP 2007-716229	A3	20070103
EP 2007-119432	A3	20071026
US 2009-404130	A	20090313
EP 2009-155292	A3	20090316
US 2009-631728	A	20091204
AU 2010-224356	A3	20100921
AU 2011-201225	A3	20110318
AU 2011-202712	A3	20110607
AU 2011-213796	A3	20110819
AU 2012-265607	A3	20121219

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): CASREACT 155:615800
OS.CITING REF COUNT: 11 THERE ARE 11 CAPLUS RECORDS THAT CITE THIS RECORD (11 CITINGS)
REFERENCE COUNT: 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 9 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB Disclosed is a process for the manufacture of HFO 1234yf from TCP in three integrated steps that include hydrofluorination of TCP (tetrachloropropene) to HCFC 1233xf in the vapor phase followed by hydrofluorination of HCFC 1233xf to HCFC 244bb in the liquid phase which is then followed by dehydrochlorination in liquid or vapor phase to produce HFO 1234yf. The vapor phase hydrofluorination is carried out at a higher pressure than the liquid phase hydrofluorination, thereby eliminating the need for compression and/or intermediate recovery. Also, any HCl generated from this reaction is fed to the liquid phase hydrofluorination section to promote agitation and mixing. This results in a more economical process from an initial capital and operating cost vs. conducting the 3-steps sequentially.
ACCESSION NUMBER: 2011:593099 CAPLUS
DOCUMENT NUMBER: 154:543144
TITLE: Integrated process for fluoroolefin production from tetrachloropropene
INVENTOR(S): Kopkalli, Haluk; Chiu, Yuon; Cottrell, Stephen A.; Tung, Hsueh Sung; Ulrich, Kevin D.
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: PCT Int. Appl., 20pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2011056441	A2	20110512	WO 2010-US53486	20101021
WO 2011056441	A3	20110915		

W: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,

CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG,
ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP,
KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA,
MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE,
PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV,
SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW
RW: AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR,
HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS,
SE, SI, SK, SM, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,
MR, NE, SN, TD, TG, BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL,
SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

US 20110105807	A1	20110505	US 2009-611288	20091103
CN 102656132	A	20120905	CN 2010-80049776	20101021
EP 2496541	A2	20120912	EP 2010-828789	20101021

R: AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR,
HU, IE, IS, IT, LI, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO,
RS, SE, SI, SK, SM, TR

JP 2013510148	T	20130321	JP 2012-537902	20101021
MX 2012005136	A	20120523	MX 2012-5136	20120502

PRIORITY APPLN. INFO.: US 2009-611288 A 20091103
WO 2010-US53486 W 20101021

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): CASREACT 154:543144

L11 ANSWER 10 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN

AB Disclosed is a process for the manufacture of HFO 1234yf from TCP in three integrated steps that include hydrofluorination of TCP (tetrachloropropene) to HCFC 1233xf in the vapor phase followed by hydrofluorination of HCFC 1233xf to HCFC 244bb in the liquid phase which is then followed by dehydrochlorination in liquid or vapor phase to produce HFO 1234yf. The vapor phase hydrofluorination is carried out at a higher pressure than the liquid phase hydrofluorination, thereby eliminating the need for compression and/or intermediate recovery. Also, any HCl generated from this reaction is fed to the liquid phase hydrofluorination section to promote agitation and mixing. This results in a more economical process from an initial capital and operating cost vs. conducting the 3-steps sequentially.

ACCESSION NUMBER: 2011:562736 CAPLUS
DOCUMENT NUMBER: 154:513896
TITLE: Integrated process for fluoroolefin production
INVENTOR(S): Kopkalli, Haluk; Chiu, Yuon; Cottrell, Stephen A.; Tung, Hsueh Sung; Uhrich, Kevin D.
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: U.S. Pat. Appl. Publ., 7pp.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 20110105807	A1	20110505	US 2009-611288	20091103
WO 2011056441	A2	20110512	WO 2010-US53486	20101021
WO 2011056441	A3	20110915		

W: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG,
ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP,
KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA,
MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE,
PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV,
SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW

RW: AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM

CN 102656132	A	20120905	CN 2010-80049776		20101021
EP 2496541	A2	20120912	EP 2010-828789		20101021
R: AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LI, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR					
JP 2013510148	T	20130321	JP 2012-537902		20101021
MX 2012005136	A	20120523	MX 2012-5136		20120502
PRIORITY APPLN. INFO.:			US 2009-611288	A	20091103
			WO 2010-US53486	W	20101021

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OS.CITING REF COUNT: 6 THERE ARE 6 CAPLUS RECORDS THAT CITE THIS RECORD (6 CITINGS)

L11 ANSWER 11 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB The manufacture of the HFO trans-1,3,3,3-tetrafluoropropene (HFO trans-1234ze) is shown. More particularly, a process for the manufacture of the HFO trans-1234ze occurs by first dehydrofluorinating 1,1,1,3,3-pentafluoropropane to produce a mixture of cis-1,3,3,3-tetrafluoropropene, trans-1,3,3,3-tetrafluoropropene, and HF. Then optionally recovering HF and then recovering trans-1,3,3,3-tetrafluoropropene.

ACCESSION NUMBER: 2008:252481 CAPLUS
DOCUMENT NUMBER: 148:287184
TITLE: Production of hfo trans-1234ze from hfc-245fa
INVENTOR(S): Wang, Haiyou; Tung, Hsueh Sung
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: U.S. Pat. Appl. Publ., 8 pp.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 20080051611	A1	20080228	US 2007-775318	20070710
US 8067650	B2	20111129		
CA 2598386	A1	20080224	CA 2007-2598386	20070823
CN 101265155	A	20080917	CN 2007-10185757	20070823
MX 2007010287	A	20081028	MX 2007-10287	20070823
KR 2008018851	A	20080228	KR 2007-85689	20070824
JP 2008150356	A	20080703	JP 2007-218239	20070824
EP 2014637	A1	20090114	EP 2007-253347	20070824
R: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR, AL, BA, HR, MK, RS				
PRIORITY APPLN. INFO.:			US 2006-839873P	P 20060824
			US 2007-775318	A 20070710

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): CASREACT 148:287184
OS.CITING REF COUNT: 1 THERE ARE 1 CAPLUS RECORDS THAT CITE THIS RECORD (1 CITINGS)

L11 ANSWER 12 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB An integrated process for the manufacture of HFO trans-1,3,3,3-tetrafluoropropene (HFO trans-1234ze) by first catalytically dehydrofluorinating 1,1,1,3,3-pentafluoropropane to produce a mixture of

cis-1,3,3,3-tetrafluoropropene, trans-1,3,3,3-tetrafluoropropene, and HF. Then optionally recovering HF, catalytically isomerizing cis-1234ze into trans-1234ze, and recovering trans-1,3,3,3-tetrafluoropropene.

ACCESSION NUMBER: 2008:252474 CAPLUS
DOCUMENT NUMBER: 148:287183
TITLE: Integrated HFC trans-1234ze manufacture process
INVENTOR(S): Wang, Haiyou; Tung, Hsueh Sung; Chiu, Yuon; Cerri, Gustavo; Cottrell, Stephen A.
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: U.S. Pat. Appl. Publ., 7 pp.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 20080051610	A1	20080228	US 2007-657354	20070124
US 7485760	B2	20090203		
CA 2598382	A1	20080224	CA 2007-2598382	20070823
EP 1900716	A1	20080319	EP 2007-253337	20070823
EP 1900716	B1	20121031		
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JP 2008069147	A	20080327	JP 2007-216914	20070823
CN 101293809	A	20081029	CN 2007-10185733	20070823
MX 2007010292	A	20090219	MX 2007-10292	20070823
EP 2295393	A1	20110316	EP 2010-184656	20070823
R: DE, ES, FR, GB, IT				
EP 2322493	A1	20110518	EP 2010-184861	20070823
R: DE, ES, FR, GB, IT				
ES 2397377	T3	20130306	ES 2007-253337	20070823
KR 2008018847	A	20080228	KR 2007-85594	20070824
US 20090118555	A1	20090507	US 2009-348538	20090105
US 7638660	B2	20091229		

PRIORITY APPLN. INFO.:	US 2006-839874P	P	20060824
	US 2007-657354	A	20070124
	EP 2007-253337	A3	20070823

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): CASREACT 148:287183
OS.CITING REF COUNT: 4 THERE ARE 4 CAPLUS RECORDS THAT CITE THIS RECORD (5 CITINGS)
REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 13 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB A review. The hydroformylation reaction is an increasingly important chemical synthesis route, as it is one of the few reactions through which a single carbon atom can be added onto a long chain species. The combination of a high volume of hydroformylation products produced com., the growing importance of chiral synthesis in pharmaceutical applications, and an increasing awareness of energy use and environmental constraints has led to extensive evaluations of hydroformylation reactions in benign reaction solvents, and in particular, supercrit. carbon dioxide (scCO2). Since the catalysts used are most often homogeneous in nature, dissolved into the solvent or reactant/product mixture, the use of scCO2 not only improves the environmental profile of hydroformylation processes but also improves the ability to recover the often expensive rhodium-based catalysts. The current review describes recent developments in the design of catalysts for hydroformylation in scCO2, in the use of these catalysts

for hydroformylation of α-olefins to form linear aldehydes and for asym. hydroformylation of styrene, and the effect of the supercrit. fluid solvent on these reactions.

ACCESSION NUMBER: 2006:1019714 CAPLUS
DOCUMENT NUMBER: 147:54395
TITLE: Hydroformylation in supercritical carbon dioxide: Catalysis and benign solvents
AUTHOR(S): Bektesevic, Selma; Kleman, Angela M.; Marteel-Parrish, Anne E.; Abraham, Martin A.
CORPORATE SOURCE: Department of Chemical and Environmental Engineering, University of Toledo, Toledo, OH, 43606, USA
SOURCE: Journal of Supercritical Fluids (2006), 38(2), 232-241 CODEN: JSFLEH; ISSN: 0896-8446
PUBLISHER: Elsevier B.V.
DOCUMENT TYPE: Journal; General Review
LANGUAGE: English
OS.CITING REF COUNT: 20 THERE ARE 20 CAPLUS RECORDS THAT CITE THIS RECORD (21 CITINGS)
REFERENCE COUNT: 76 THERE ARE 76 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 14 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN

AB A process for preparing a haloalkane comprises: (a) contacting a haloalkane starting material (e.g., tetrachloromethane) with an alkene (e.g., ethylene) in the presence of an effective amount of a catalyst complex (e.g., cuprous chloride and laurylamine) under conditions effective to facilitate an addition reaction and to form a product stream comprising a haloalkane product (e.g., 1,1,1,3-tetrachloropropane) from the addition reaction, where the catalyst complex has a b.p. higher than that of the haloalkane product; and (b) recovering the haloalkane product from the product stream. Process flow diagrams are presented.

ACCESSION NUMBER: 2006:540996 CAPLUS
DOCUMENT NUMBER: 145:45701
TITLE: Continuous catalytic alkene haloalkylation process for preparing halogenated alkanes
INVENTOR(S): Tung, Hsueh Sung
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: U.S. Pat. Appl. Publ., 8 pp. CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 20060122441	A1	20060608	US 2004-7036	20041208
US 7102041	B2	20060905		
PRIORITY APPLN. INFO.:			US 2004-7036	20041208

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): CASREACT 145:45701
REFERENCE COUNT: 10 THERE ARE 10 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 15 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN

AB A process for the preparation of a hydrofluorocarbon comprises: (a) reacting at least one hydrochlorocarbon (e.g., methylene chloride) with hydrogen fluoride in the presence of a fluorination catalyst (e.g., antimony pentachloride), where the hydrogen fluoride-hydrochlorocarbon molar ratio is ≥15:1, resp.; (b) optionally recycling a portion of any unreacted HF back to step (a); (c) optionally removing any HCl produced by step (a); and (d) recovering the hydrofluorocarbon (e.g.,

difluoromethane).

ACCESSION NUMBER: 2004:1019828 CAPLUS
DOCUMENT NUMBER: 142:8270
TITLE: Catalytic fluorination method for the manufacture of hydrofluorocarbons from hydrochlorocarbons and hydrogen fluoride
INVENTOR(S): Tung, Hsueh Sung; Marks, Chad L.; Cottrell, Stephen A.
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: U.S. Pat. Appl. Publ., 5 pp.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 20040236160	A1	20041125	US 2003-444610	20030523
US 7214839	B2	20070508		
WO 2004106271	A2	20041209	WO 2004-US16231	20040521
WO 2004106271	A3	20050303		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
EP 1628943	A2	20060301	EP 2004-753117	20040521
R: DE, ES, FR, GB, IT				
CN 1826304	A	20060830	CN 2004-80020984	20040521
JP 2007500228	T	20070111	JP 2006-533341	20040521

PRIORITY APPLN. INFO.: US 2003-444610 A 20030523
WO 2004-US16231 W 20040521
ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): CASREACT 142:8270
REFERENCE COUNT: 14 THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 16 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB The hydroformylation of alkenes is a major com. process used for the production of oxygenated organic compds. When the hydroformylation reaction is performed using a homogeneous catalyst, an organic or aqueous solvent is employed, and a significant effort must be expended to recover the catalyst so it can be recycled. Development of a selective heterogeneous catalyst would allow simplification of the process design in an integrated system that minimizes waste generation. Recent studies have shown that supercrit. carbon dioxide (scCO2) as a reaction solvent offers optimal environmental performance and presents advantages for ease of product separation In particular, we have considered the conversion of 1-hexene to heptanal using rhodium- and platinum-phosphine catalysts tethered to supports insol. in scCO2 to demonstrate the advantages and to understand the limitations of a solid-catalyzed process. One of the historical limitations of supported catalysts is the inability to control product regioselectivity. To address this concern, we have developed tethered catalysts with phosphinated silica and controlled pore size MCM-41 and MCM-20 supports that provide improved regioselectivity and conversion relative to their nonporous equivalent Platinum catalysts supported on

MCM-type supports were the most regioselective whereas the analogous rhodium catalysts were the most active for hydroformylation of 1-hexene in scCO2.

ACCESSION NUMBER: 2003:829506 CAPLUS
DOCUMENT NUMBER: 140:43744
TITLE: Hydroformylation of 1-Hexene in Supercritical Carbon Dioxide: Characterization, Activity, and Regioselectivity Studies
AUTHOR(S): Marteel, Anne E.; Tack, Timothy T.; Bektesevic, Selma; Davies, Julian A.; Mason, Mark R.; Abraham, Martin A.
CORPORATE SOURCE: Department of Chemistry and Department of Chemical and Environmental Engineering, The University of Toledo, Toledo, OH, 43606, USA
SOURCE: Environmental Science and Technology (2003), 37(23), 5424-5431
CODEN: ESTHAG; ISSN: 0013-936X
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OS.CITING REF COUNT: 10 THERE ARE 10 CAPLUS RECORDS THAT CITE THIS RECORD (10 CITINGS)
REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 17 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB An azeotrope-like composition, consisting of 1,1,1,3,3-pentafluorobutane (HFC-365mfc) and HF, has a vapor pressure of 15-22 psia at 20.2° and 29-36 psia at 40.2°, and a preferred composition of 90-96 weight% HFC-365mfc and 4-10 weight% HF. The separation of HFC-365mfc from HF can be carried out in two steps: (1) distilling the azeotropic mixture at a first pressure to produce a first overhead stream enriched in either HFC-365mfc or HF and a first bottoms stream enriched in the other component, followed by (2) redistg. the first overheads at a second pressure to produce a second overheads enriched in the component enriched in the first bottoms stream, and a second bottoms stream enriched in the component enriched in the first overheads. The azeotropic compns. at 20.2° and 40.2° are 96:4 and 92:8 weight% ratio HFC-365mfc-HF, resp. HFC-365mfc is useful as a nontoxic, zero-ozone-depleting fluorocarbon which can be used as a solvent, blowing agent, refrigerant, cleaning agent, and propellant for sprays and aerosols.

ACCESSION NUMBER: 2002:946166 CAPLUS
DOCUMENT NUMBER: 138:26367
TITLE: Separation of pentafluorobutane-HF azeotrope mixtures for recovery of 1,1,1,3,3-pentafluorobutane as potential novel refrigerants, aerosol propellants, polymer blowing agent, and cleaning solvent.
INVENTOR(S): Pham, Hang T.; Singh, Rajiv R.; Tung, Hsueh S.
PATENT ASSIGNEE(S): Honeywell International Inc., USA
SOURCE: PCT Int. Appl., 12 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2002098529	A1	20021212	WO 2002-US17246	20020603

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,

LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH,
PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ,
UA, UG, US, UZ, VN, YU, ZA, ZM, ZW
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, CH,
CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR,
BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

AU	2002310253	A1	20021216	AU 2002-310253	20020603
US	20030009065	A1	20030109	US 2002-160673	20020603
US	6673264	B2	20040106		
EP	1425076	A1	20040609	EP 2002-737315	20020603
EP	1425076	B1	20090415		

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
IE, SI, LT, LV, FI, RO, MK, CY, AL, TR

CN	1549739	A	20041124	CN 2002-810803	20020603
CN	100467093	C	20090311		
JP	2005503249	T	20050203	JP 2003-501565	20020603
JP	4511827	B2	20100728		
CN	101270029	A	20080924	CN 2008-10009657	20020603
AT	428671	T	20090515	AT 2002-737315	20020603
CN	101462924	A	20090624	CN 2009-10003603	20020603
ES	2220248	T3	20090715	ES 2002-737315	20020603
EP	2093187	A1	20090826	EP 2009-157436	20020603

R: AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LI, LU, MC,
NL, PT, SE, TR

US	20040084295	A1	20040506	US 2003-684786	20031014
US	7361795	B2	20080422		
US	20070278087	A1	20071206	US 2007-842652	20070821
US	7781626	B2	20100824		

PRIORITY APPLN. INFO.:	US 2001-295049P	P	20010601
	CN 2002-810803	A3	20020603
	EP 2002-737315	A3	20020603
	US 2002-160673	A3	20020603
	WO 2002-US17246	W	20020603
	US 2003-684786	A3	20031014

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT

OS.CITING REF COUNT:	1	THERE ARE 1 CAPLUS RECORDS THAT CITE THIS RECORD (1 CITINGS)
REFERENCE COUNT:	4	THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 18 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN

AB Difluoromethane (i.e., HFC-32; I) is prepared in high yield and selectivity by: (A) preheating a mixture of HF (II) and Cl2CH2 (III) to form a vaporized and superheater composition; (B) reacting this superheated composition in the presence of a fluorination catalyst (e.g., Cr2O3/Al2O3) to form a product stream containing F2CH2, ClFCH2 (IV), HCl (V), Cl2CH2, and HF; (C) distilling the product stream to produce a high-boiling stream comprising II, III, and IV, and a low-boiling stream comprising I, II, and V; and (D) recovering substantially pure I from the low-boiling distillation fraction.

ACCESSION NUMBER:	1997:281849 CAPLUS
DOCUMENT NUMBER:	126:263837
ORIGINAL REFERENCE NO.:	126:51101a,51104a
TITLE:	Vapor-phase process and catalysts for the production of difluoromethane from hydrogen fluoride and dichloromethane
INVENTOR(S):	Clemmer, Paul Gene; Smith, Addison Miles; Tung, Hsueh Sung; Bass, John Stephen
PATENT ASSIGNEE(S):	AlliedSignal Inc., USA
SOURCE:	PCT Int. Appl., 14 pp. CODEN: PIXXD2
DOCUMENT TYPE:	Patent

LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9711043	A1	19970327	WO 1996-US14734	19960913
W: AL, AU, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LK, LR, LT, LV, MG, MK, MN, MW, MX, NO, NZ, PL, RO, SD, SG, SI, SK, TR, TT, UA, UZ, VN, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: KE, LS, MW, SD, SZ, UG, AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG				
US 5763708	A	19980609	US 1995-530649	19950920
CA 2232596	A1	19970327	CA 1996-2232596	19960913
CA 2232596	C	20080415		
AU 9669775	A	19970409	AU 1996-69775	19960913
AU 702786	B2	19990304		
EP 854848	A1	19980729	EP 1996-930874	19960913
EP 854848	B1	20030319		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, NL, SE, PT, IE				
CN 1201446	A	19981209	CN 1996-198176	19960913
BR 9610669	A	19990713	BR 1996-10669	19960913
HU 9901285	A2	19990728	HU 1999-1285	19960913
HU 9901285	A3	20000228		
JP 11512454	T	19991026	JP 1997-512794	19960913
AT 234797	T	20030415	AT 1996-930874	19960913
PT 854848	E	20030731	PT 1996-930874	19960913
ES 2193261	T3	20031101	ES 1996-930874	19960913
TW 388751	B	20000501	TW 1996-111366	19960917
US 6844474	B1	20050118	US 1997-959748	19971028
US 6365580	B1	20020402	US 1999-425150	19991021
US 20050004408	A1	20050106	US 2004-896905	20040723

PRIORITY APPLN. INFO.:
US 1995-530649 A 19950920
WO 1996-US14734 W 19960913
US 1997-959748 A3 19971028

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): CASREACT 126:263837
OS.CITING REF COUNT: 9 THERE ARE 9 CAPLUS RECORDS THAT CITE THIS RECORD (10 CITINGS)
REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 19 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB The process comprises (a) subjecting a binary azeotrope to a distillation step in which most of one of the binary components is removed as distillate (distillate 1) with the bottoms (bottoms 1) enriched in the other component; (b) subjecting distillate 1 to ≥1 addnl. distillation step at a different pressure in which most of the component recovered as bottoms 1 is removed as distillate 2 with the bottoms 2 enriched in the component enriched in distillate 1; and (c) recovering the desired purified component. The invention is particularly useful in the purification of pentafluoroethane in a pentafluoroethane/chloropentafluoroethane azeotrope.
ACCESSION NUMBER: 1995:285637 CAPLUS
DOCUMENT NUMBER: 122:58823
ORIGINAL REFERENCE NO.: 122:11313a,11316a
TITLE: Purification of a component of a binary azeotrope by multiple distillations
INVENTOR(S): Clemmer, Paul Gene; Tung, Hsueh Sung; Smith, Addison Miles
PATENT ASSIGNEE(S): AlliedSignal Inc., USA

SOURCE: PCT Int. Appl., 16 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9419301	A1	19940901	WO 1994-US1117	19940131
W: JP, KR				
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE				
US 5346595	A	19940913	US 1993-23827	19930223
EP 686137	A1	19951213	EP 1994-907385	19940131
EP 686137	B1	19990728		
R: DE, ES, FR, GB, IT, NL				
JP 08502758	T	19960326	JP 1994-518991	19940131
JP 2800851	B2	19980921		
ES 2136190	T3	19991116	ES 1994-907385	19940131

PRIORITY APPLN. INFO.: US 1993-23827 A 19930223
WO 1994-US1117 W 19940131
ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OS.CITING REF COUNT: 4 THERE ARE 4 CAPLUS RECORDS THAT CITE THIS RECORD (5 CITINGS)
REFERENCE COUNT: 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L11 ANSWER 20 OF 20 CAPLUS COPYRIGHT 2013 ACS on STN
AB Qual. investigations of the mechanisms of photochem. decomposition of diphenylpermethyltitanocene and -zirconocene were made. Reductive elimination as well as homolytic cleavage of metal-C σ bonds are the 2 major pathways. When C6D6 was used as the solvent for photolysis of diphenylpermethyltitanocene, PhPh and PhC6D5 were found in 36:1 ratio, indicating that reductive elimination was the much more favorable process. However, in the case of diphenylpermethylzirconocene, PhPh and PhC6D5 were formed in 1:3 ratio, indicating that the homolytic photocleavage of the σ bonds predominated. In the presence of CO, moderately large amts. of the dicarbonylpermethylmetallocenes were found, suggesting that the permethylmetallocenes were the intermediates. The discovery of pentamethylcyclopentadiene and 2,3,4,5-tetramethylfulvene in the recovered solvent indicated further photodecompn. of permethylmetallocene. Consequently, another intermediate, [(C5Me5)(C5Me4CH2)M], was proposed.
ACCESSION NUMBER: 1982:104434 CAPLUS
DOCUMENT NUMBER: 96:104434
ORIGINAL REFERENCE NO.: 96:17157a,17160a
TITLE: Photochemical decomposition of (diphenyl)bis(η5-cyclopentadienyl)titanium, (diphenyl(bis(η5-pentamethylcyclopentadienyl)titanium and the zirconium analogs
AUTHOR(S): Tung, Hsueh Sung; Brubaker, Carl H., Jr.
CORPORATE SOURCE: Dep. Chem., Michigan State Univ., East Lansing, MI, 48824, USA
SOURCE: Inorganica Chimica Acta (1981), 52(2), 197-204
CODEN: ICHAA3; ISSN: 0020-1693
DOCUMENT TYPE: Journal
LANGUAGE: English
OS.CITING REF COUNT: 8 THERE ARE 8 CAPLUS RECORDS THAT CITE THIS RECORD (8 CITINGS)

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     FILE 'CAPLUS' ENTERED AT 00:38:42 ON 03 JUN 2013
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L5             0 SEA FILE=CAPLUS SPE=ON  PLU=ON  L4 AND RECOVERY
L6            22 SEA FILE=CAPLUS SPE=ON  PLU=ON  BEKTESEVIC SELMA/AU
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L8           187 SEA FILE=CAPLUS SPE=ON  PLU=ON  ("TUNG HSUEH"/AU OR "TUNG
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                 "TUNG HSUEH SUNG HARRY"/AU)
                 E KOPKALLI HALUK/AU
L9            23 SEA FILE=CAPLUS SPE=ON  PLU=ON  "KOPKALLI HALUK"/AU
L10          204 SEA FILE=CAPLUS SPE=ON  PLU=ON  L6 OR L8 OR L9
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                 D L11 ABS IBIB HITSTR 1-
COST IN U.S. DOLLARS                          SINCE FILE      TOTAL
                                                   ENTRY    SESSION
FULL ESTIMATED COST                                99.73     173.05

STN INTERNATIONAL LOGOFF AT 00:45:56 ON 03 JUN 2013
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	**Selma Bektesevic, et al.**		Examiner: **Clinton A. Brooks**
Application No.:	**13/229,016**	Conf. No. **8706**	Group Art Unit: **1621**
Filed:	**September 9, 2011**		Attorney Docket No. **H0024680**

Title: **INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS**

FILED ELECTRONICALLY

Mail Stop: Amendments
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

RESPONSE TO NON-FINAL OFFICE ACTION OF JUNE 6, 2013

Sir:

This Reply is in response to the Non-Final Office Action of June 6, 2013 and conforms to the submission requirements. Reconsideration in view of the amendments herein is respectfully requested. Applicants believe that no fees are currently due to further the prosecution of this application. However, if any fees are necessary, please charge such fees to Deposit Account No. 50-1943.

Amendments to the claims begin on page 2 of this correspondence.

Remarks begin on page 9.

AMENDMENTS TO THE CLAIMS

The following listing of the claims replaces all prior versions and listings:

A Listing of the Claims

1. (Original) A method for producing at least one fluorinated olefin comprising:

   a. hydrogenating a starting material stream comprising at least one alkene according to Formula (I):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_zCX{=}CH_mX_{2-m} \qquad (I)$$

   by contacting said starting material with a reducing agent to produce an intermediate product stream comprising at least one alkane according to Formula (II):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_zCHXCH_{m+1}X_{2-m} \qquad (II)$$

   where:

   each X is independently Cl, F, I or Br, provided that at least two Xs are F;

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

   each R^1 is independently H, Cl, F, I, Br or unsubstituted or halogen substituted methyl or ethyl radical;

   each R_2 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 0, 1 or 2, provided that a+b = 2;

   m is 0, 1 or 2; and

   z is 0, 1, 2 or 3;

b. optionally, separating said intermediate product stream into a plurality of intermediate product streams, said plurality of intermediate product streams comprising two or more streams selected from the group consisting of a first stream rich in at least a first alkane according to Formula II, a seconds stream rich in at least a second alkane according to Formula II, and an alkane recycle stream;

c. dehydrofluorinating, in the presence of a dehydrohalogenating agent, at least a portion of said intermediate process stream from step (a) or said plurality of intermediate process streams of step (b) to produce an alkene product stream comprising 1,1,1,2,3-pentafluoropropene and at least one additional alkene having a lower degree of fluorine substitution compared to the degree of fluorination of the compound of formula (I); and

d. withdrawing from a dehydrofluorinated product stream a product reaction stream comprising spent dehydrohalogenating agent; and

e. recovering spent dehydrohalogenating agent.

2. (Original) The method of claim 1 wherein said additional alkene is a compound according to formula (III):

$$(CX_nY_{3-n})(CR^1_aR^2_b)_ZCX{=}CH_{m+1}X_{1-m} \text{ (III)}$$

where each of X, Y, R^1, R^2, n, a, and b is the same value as in formula (I) and m is 0 or 1.

3. (Original) The method of claim 2 wherein Z is 0.

4. (Original) The method of claim 3 wherein m is 0 or 1.

5. (Original) The method of claim 4 wherein said n is 3.

6. (Original) The method of claim 5 wherein X is F.

7. (Original) The method of claim 1 wherein said reducing agent is H_2.

8. (Previously presented) The method of claim 1 wherein said starting material stream comprises hexafluoropropylene and said additional alkene is 2,3,3,3-tetrafluoropropene.

9. (Original) The method of claim 1 wherein the dehydrohalogenating agent is selected from the group consisting of KOH, NaOH, $Ca(OH)_2$, LiOH, $Mg(OH)_2$, CaO, and combinations thereof.

10. (Previously presented) A method for producing 2,3,3,3-tetrafluoropropene comprising:

a. hydrogenating a starting material stream comprising hexafluoropropylene by contacting said starting material stream with a reducing agent in a hydrogenation reactor to produce an intermediate stream comprising 1,1,1,2,3-pentafluoropropane or 1,1,1,2,3,3-hexafluoropropane;

b. dehydrofluorinating, in the presence of a dehydrohalogenating agent, said 1,1,1,2,3-pentafluoropropane or said 1,1,1,2,3,3-hexafluoropropane in a dehydrofluorination reactor to produce a product stream comprising 2,3,3,3-tetrafluoropropene or 1,2,3,3,3-pentafluoropropene;

c. withdrawing from the product stream a second product stream comprising spent dehydrohalogenating agent; and

d. recovering spent dehydrohalogenating agent.

11. (Currently amended) The ~~process~~ method of claim 10 wherein the second product stream further comprises one or more dissolved organics.

12. (Currently amended) The ~~process~~ method of claim 11 wherein the dissolved organics are selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,2,3-pentafluoropropane (HFC-245eb), and combinations thereof.

13. (Currently amended) The ~~process~~ method of claim 10 wherein the spent dehydrohalogenating agent is purified using at least one separation method.

14. (Currently amended) The ~~process~~ method of claim 13 wherein the separation method is selected from the group consisting of distillation or phase separation.

15. (Currently amended) The ~~process~~ method of claim 10 further comprising, optionally, concentrating the purified dehydrohalogenating agent and recycling it back to the dehydrohalogenation reaction.

16. (Currently amended) The ~~process~~ method of claim 10 wherein the reaction stream further comprises by-product salts of the dehydrohalogenating agent.

17. (Currently amended) The ~~process~~ method of claim 16 further comprising converting the by-product salts to the dehydrohalogenating agent.

18. (Currently amended) The ~~process~~ method of claim 16 wherein the dehydrohalogenating agent is KOH and the by-product salt is KF.

19. (Currently amended) The ~~process~~ method of claim 18 further comprising, optionally, concentrating the converted KOH and recycling it back to the dehydrohalogenation reaction.

20. (Currently amended) The ~~process~~ method of claim 18 further comprising converting KF to KOH in the presence of $Ca(OH)_2$.

21. (Original) A process for the manufacture of a fluoroolefin comprising:

(a) dehydrohalogenating a haloalkane in the presence of KOH to produce a haloalkene;

(b) withdrawing a reaction stream comprising spent KOH; and

(c) recovering spent KOH.

22. (Original) The process of claim 21 wherein the haloalkane is comprised of a compound of formula (IIA):

$$(CX_nY_{3-n})CHXCH_{m+1}X_{2-m} \quad (IIA)$$

wherein each X is independently selected from the group consisting of Cl, F, I and Br; each Y is independently selected from the group consisting of H, Cl, F, I, and Br; n is 1,2, or 3; and m is 0, 1 or 2.

23. (Original) The process of claim 22 wherein the haloalkane is 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb).

24. (Original) The process of claim 21 wherein the haloalkene is comprised of a compound of formula (IIIA):

$$(CX_nY_{3-n})CX{=}CH_{m+1}X_{1-m} \quad (IIIA)$$

wherein each X is independently selected from the group consisting of Cl, F, I and Br; each Y is independently selected from the group consisting of H, Cl, F, I, and Br; n is 1,2, or 3; and m is 0 or 1.

25. (Previously presented) The process of claim 24 wherein the haloalkene is 2,3,3,3-tetrafluoropropene (HFO-1234yf) or 1,2,3,3,3-pentafluoropropene (HFO-1225ye).

26. (Original) The process of claim 21 wherein the dehydrohalogenation occurs using a continuously stirred tank reactor.

27. (Original) The process of claim 21 wherein the spent KOH is withdrawn from the reactor continuously or intermittently.

28. (Original) The process of claim 21 wherein the reaction stream further comprises a dissolved organics.

29. (Original) The process of claim 28 wherein the dissolved organics are selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb).

30. (Original) The process of claim 21 wherein the spent KOH is purified using at least one separation method.

31. (Original) The process of claim 30 wherein the separation method is selected from the group consisting of distillation or phase separation.

32. (Original) The process of claim 21 further comprising, optionally, concentrating the purified KOH and recycling it back to the dehydrohalogenation reaction.

33. (Original) The process of claim 21 wherein the reaction stream further comprises KF.

34. (Currently amended) The process of claim 33 further comprising converting KF to KOH in the presence of $Ca(OH)_2$.

35. (Original) The process of claim 34 further comprising, optionally, concentrating the converted KOH and recycling it back to the dehydrohalogenation reaction.

36. (Previously presented) A process for the manufacture of a fluoroolefin comprising:

(a) dehydrohalogenating 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb) in the presence of KOH to produce 2,3,3,3-tetrafluoropropene (HFO-1234yf) or 1,2,3,3,3-pentafluoropropene (HFO-1225ye);

(b) withdrawing a reaction stream comprising spent KOH; and

(c) recovering spent KOH.

37. (Original) The process of claim 36 wherein the dehydrohalogenation occurs using a continuously stirred tank reactor.

38. (Original) The process of claim 36 wherein the spent KOH is withdrawn from the reactor continuously or intermittently.

39. (Original) The process of claim 36 wherein the reaction stream further comprises a dissolved organics.

40. (Original) The process of claim 37 wherein the dissolved organics are selected from the group consisting of 1,1,1,2,3,3-hexafluoropropane (HFC-236ea) or 1,1,1,2,3-pentafluoropropane (HFC-245eb).

41. (Original) The process of claim 36 wherein the spent KOH is purified using at least one separation method.

42. (Original) The process of claim 41 wherein the separation method is selected from the group consisting of distillation or phase separation.

43. (Original) The process of claim 36 further comprising, optionally, concentrating the purified KOH and recycling it back to the dehydrohalogenation reaction.

44. (Original) The process of claim 36 wherein the reaction stream further comprises KF.

45. (Original) The process of claim 44 further comprising purifying KF from the reaction stream.

46. (Original) The process of claim 36 further comprising converting KF to KOH in the presence of $Ca(OH)_2$, optionally, concentrating the KOH and recycling it back to the dehydrohalogenation reaction.

REMARKS

Applicants respectfully assert that the instant claims, as amended, are in a condition for allowance and respectfully request allowance of the same in view of the arguments provided below.

A. Status of the Claims

Claims 11-20 were rejected under 35 U.S.C. 112(b) (35 U.S.C. 112, second paragraph – pre-AIA) as being indefinite for failing to particularly point out and distinctly claim the subject matter of the invention. Specifically, it was argued that the preamble of these claims, reciting "the process," lacks antecedent basis. The claim from which these claims depend recites "a method."

Claims 1-10 and 21-46 were indicated as being allowable.

Claims 11-20 are amended, as discussed below. Claim 34 is amended to correct a typographical error and amend its dependency from claim 3 to claim 33.

B. Rejection under 35 U.S.C. 112

Applicants respectfully thank the Examiner for the indication of allowability of claims 1-10 and 21-46.

Claims 11-20 are amended herein to overcome the rejection under 35 U.S.C. 112. That is, the term "the process" in each of these claims has been removed and replaced with the term "the method." Thus, claims 11-20 comport with the preamble of the claim from which they depend, claim 10.

Applicants respectfully submit that claims 1-46 are all allowable on the basis of these amendments. Reconsideration in view of the foregoing is respectfully requested.

CONCLUSION

The pending claims are believed to be in condition for allowance, and an early notice thereof is earnestly solicited.

The Office is invited to contact Applicants' undersigned counsel by telephone in order to further the prosecution of this case in any way.

Respectfully submitted,

Dated: August 29, 2013

/J. Eric Sumner/
J. Eric Sumner
Registration No. 58,699
Eagleview Corporate Center
747 Constitution Drive, Suite 100
Exton, PA 19341
Tel: 610-458-6712
Fax: 610-458-7337
Email: esumner@foxrothschild.com

Electronic Acknowledgement Receipt

EFS ID:	16721808
Application Number:	13229016
International Application Number:	
Confirmation Number:	8706
Title of Invention:	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS
First Named Inventor/Applicant Name:	SELMA BEKTESEVIC
Customer Number:	91970
Filer:	John Eric Sumner/Michele Greenberg
Filer Authorized By:	John Eric Sumner
Attorney Docket Number:	H0024680-4511
Receipt Date:	29-AUG-2013
Filing Date:	09-SEP-2011
Time Stamp:	14:44:28
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		Response_to_Non_Final_OA__H0024680_4511__P36241A_US.PDF	113894 9f7a278462243de79eff45f4e7f66750c85df564	yes	10

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Amendment/Req. Reconsideration-After Non-Final Reject	1	1
	Claims	2	8
	Applicant Arguments/Remarks Made in an Amendment	9	10
Warnings:			
Information:			
	Total Files Size (in bytes):	113894	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

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.

PTO/SB/06 (09-11)
Approved for use through 1/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 13/229,016	Filing Date 09/09/2011	☐ To be Mailed

ENTITY: ☒ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED – PART I

	(Column 1)	(Column 2)		
FOR	NUMBER FILED	NUMBER EXTRA	RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	

APPLICATION AS AMENDED – PART II

		(Column 1)		(Column 2)	(Column 3)		
	08/29/2013	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
AMENDMENT	Total (37 CFR 1.16(i))	* 46	Minus	** 46	= 0	X $80 =	0
	Independent (37 CFR 1.16(h))	* 4	Minus	***4	= 0	X $420 =	0
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	**0**

		(Column 1)		(Column 2)	(Column 3)		
		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)
AMENDMENT	Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))						
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))						
						TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

LIE
/CORALIA BETANCOURT/

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

91970 7590 12/13/2013
HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962

EXAMINER
BROOKS, CLINTON A

ART UNIT	PAPER NUMBER
1621	

DATE MAILED: 12/13/2013

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/229,016	09/09/2011	SELMA BEKTESEVIC	H0024680-4511	8706

TITLE OF INVENTION: INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1780	$300	$0	$2080	03/13/2014

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 1/2 the amount of undiscounted fees, and micro entity fees are 1/2 the amount of small entity fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed and an extra copy of the form should be submitted. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Utility patents issuing on applications filed on or after Dec. 12, 1980 may require payment of maintenance fees. It is patentee's responsibility to ensure timely payment of maintenance fees when due.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

91970 7590 12/13/2013
HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission
I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/229,016	09/09/2011	SELMA BEKTESEVIC	H0024680-4511	8706

TITLE OF INVENTION: INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1780	$300	$0	$2080	03/13/2014

EXAMINER	ART UNIT	CLASS-SUBCLASS
BROOKS, CLINTON A	1621	570-157000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).
- ❑ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.
- ❑ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) the names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) the name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.
1 _____
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. The following fee(s) are submitted:
- ❑ Issue Fee
- ❑ Publication Fee (No small entity discount permitted)
- ❑ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**
- ❑ A check is enclosed.
- ❑ Payment by credit card. Form PTO-2038 is attached.
- ❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment, to Deposit Account Number _____ (enclose an extra copy of this form).

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29	NOTE: Absent a valid certification of Micro Entity Status (see form PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
❑ Applicant asserting small entity status. See 37 CFR 1.27	NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
❑ Applicant changing to regular undiscounted fee status.	NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: The Issue Fee and Publication Fee (if required) will not be accepted from anyone other than the applicant; a registered attorney or agent; or the assignee or other party in interest as shown by the records of the United States Patent and Trademark Office.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

This collection of information is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450.

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United States Patent and Trademark Office
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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/229,016	09/09/2011	SELMA BEKTESEVIC	H0024680-4511	8706

91970 7590 12/13/2013

HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962

EXAMINER	
BROOKS, CLINTON A	

ART UNIT	PAPER NUMBER
1621	

DATE MAILED: 12/13/2013

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment to date is 69 day(s). If the issue fee is paid on the date that is three months after the mailing date of this notice and the patent issues on the Tuesday before the date that is 28 weeks (six and a half months) after the mailing date of this notice, the Patent Term Adjustment will be 69 day(s).

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notices of Allowance and Fee(s) Due mailed between October 1, 2013 and December 31, 2013

(Addendum to PTOL-85)

If the "Notice of Allowance and Fee(s) Due" has a mailing date on or after October 1, 2013 and before January 1, 2014, the following information is applicable to this application.

If the issue fee is being timely paid on or after January 1, 2014, the amount due is the issue fee and publication fee in effect January 1, 2014. On January 1, 2014, the issue fees set forth in 37 CFR 1.18 decrease significantly and the publication fee set forth in 37 CFR 1.18(d)(1) decreases to $0.

If an issue fee or publication fee has been previously paid in this application, applicant is not entitled to a refund of the difference between the amount paid and the amount in effect on January 1, 2014.

Notice of Allowability	Application No. 13/229,016	Applicant(s) BEKTESEVIC ET AL.	
	Examiner CLINTON BROOKS	Art Unit 1621	AIA (First Inventor to File) Status No

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☒ This communication is responsive to *8/29/2013*.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on_____.
2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.
3. ☒ The allowed claim(s) is/are *1-46*. As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to PPHfeedback@uspto.gov .
4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some *c) ☐ None of the:
   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____.

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).
6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date _____ .
5. ☐ Examiner's Amendment/Comment
6. ☐ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/CLINTON BROOKS/ Primary Examiner, Art Unit 1621	12/8/2013

/CB/

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	40	US-5396000-$.DID. OR US-5679875-$.DID. OR US-6031141-$.DID. OR US-6548719-$.DID. OR US-5672787-$.DID. OR US-5714655-$.DID. OR US-4876405-$.DID. OR US-5672803-$.DID. OR US-6734332-$.DID. OR US-7230146-$.DID. OR US-6369284-$.DID. OR US-7560602-$.DID. OR US-20070123741-$.DID. OR US-20060106263-$.DID. OR US-20070129579-$.DID. OR US-20040119047-$.DID. OR US-20090278075-$.DID. OR US-20090234165-$.DID. OR US-9833755-$.DID. OR US-2152031-$.DID. OR US-2935702-$.DID.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L2	2	WO-2009084703-$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L3	2	WO-2009125201-$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L4	44	L1 or L2 or L3	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L5	14	bektesevic$selma$.in.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L6	404	tung$hsueh$.in.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L7	26	kopkalli$haluk$.in.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51

L8	415	L5 or L6 or L7	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L9	0	L8 and hexaflouropropylene	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L10	20	L8 and HFP	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L11	12	L10 and 245eb	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L12	12	L11 and hydrogen	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L13	0	L12 and hydroxie	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L14	5	L12 and hydroxide	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L15	2	"8242316".pn.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L16	1	WO-2012050157-$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L17	1	WO-2012051057-$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51

L18	1	2012-B24772.NRAN.	DERWENT	OR	ON	2013/12/08 19:51
L19	1	2012-B24772.NRAN.	DERWENT	OR	ON	2013/12/08 19:51
L20	2	US-20090234165-$.did.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L21	17973	"570".clas.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L22	0	halogenating same contacting same separating same dehydrofluorinating	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L23	1	halogenating same contacting same dehydrofluorinating	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L24	4	halogenating and contacting and dehydrofluorinating	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L25	1167	1234yf	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L26	90	L25 and hexafluoropropylene	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L27	71	L26 and (pentafluoropropane or hexafluoropropane)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L28	31	L27 and hydroxide	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L29	2	"8013194".pn.	US-PGPUB;	OR	ON	2013/12/08 19:51

			USPAT; USOCR; EPO; JPO; DERWENT			
L30	17973	"570".clas.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L31	2150	L30 and (sodium adj hydroxide)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L32	69683	(sodium adj hydroxide) and recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L33	2156	(sodium adj hydroxide) with recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L34	24	L30 and L33	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L35	2	L34 and dehydrohalogenat$	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L36	61	(sodium adj hydroxide) adj recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L37	0	L36 and "570".clas.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L38	214	hydroxide adj recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L39	2	L38 and "570".clas.	US-PGPUB;	OR	ON	2013/12/08 19:51

			USPAT; USOCR; EPO; JPO; DERWENT			
L40	6	spent with KOH with recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L41	2	spent adj KOH with recovery	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L42	23	spent adj KOH	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L43	0	recycling adj KF	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L44	58	recycling with potassium with fluoride	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L45	32	recycling with (potassium adj fluoride)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:51
L46	2	"8013194".pn.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:53
L47	2	"8242316".pn.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 19:59
L48	17973	"570".clas.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 20:00
L49	1167	1234yf	US-PGPUB;	OR	ON	2013/12/08 20:00

			USPAT; USOCR; EPO; JPO; DERWENT			
L50	402	l48 and l49	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 20:01
L51	77	l50 and scrubber	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 20:01
L52	3	l51 and (scrubber same KOH same recycle)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 20:03
L60	330	570/155.ccls.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 20:35
L61	170	570/157.ccls.	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 20:35
L62	465	l60 or l61	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 20:35
L63	211	l62 and (hydroxide or KOH)	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 20:35
L64	5	l63 and (recycle same (KOH or hydroxide))	US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT	OR	ON	2013/12/08 20:35

EAST Search History (Interference)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L53	143	570/155.ccls.	USPAT; UPAD	OR	ON	2013/12/08 20:33
L54	0	570/157/ccls/	USPAT;	OR	ON	2013/12/08

			UPAD			20:33
L55	96	570/157.ccls.	USPAT; UPAD	OR	ON	2013/12/08 20:33
L56	19	l53 and l55	USPAT; UPAD	OR	ON	2013/12/08 20:33
L57	220	l53 or l55	USPAT; UPAD	OR	ON	2013/12/08 20:33
L58	47	l57 and KOH	USPAT; UPAD	OR	ON	2013/12/08 20:34
L59	1	l58 and (KOH same recycle)	USPAT; UPAD	OR	ON	2013/12/08 20:34

12/ 8/ 2013 8:41:02 PM
C:\ Users\ cbrooks2\ Documents\ EAST\ Workspaces\ 13229016\ 13229016 - keyword - ids-inventor names.wsp

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13229016	BEKTESEVIC ET AL.
	Examiner	**Art Unit**
	CLINTON BROOKS	1621

CPC						
Symbol					**Type**	**Version**
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CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
			/					
			/					

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	46	
/CLINTON BROOKS/ Primary Examiner.Art Unit 1621	12/8/2013	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	NONE

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13229016	BEKTESEVIC ET AL.
	Examiner	**Art Unit**
	CLINTON BROOKS	1621

US ORIGINAL CLASSIFICATION		INTERNATIONAL CLASSIFICATION												
CLASS	SUBCLASS	CLAIMED					NON-CLAIMED							
570	157	C	0	7	C	17 / 25 (2006.01.01)								
CROSS REFERENCE(S)		C	0	7	C	19 / 08 (2006.01.01)								
		C	0	7	C	21 / 18 (2006.01.01)								
CLASS	SUBCLASS (ONE SUBCLASS PER BLOCK)													
570	155													

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	46	
/CLINTON BROOKS/ Primary Examiner.Art Unit 1621	12/8/2013	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	NONE

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13229016	BEKTESEVIC ET AL.
	Examiner	**Art Unit**
	CLINTON BROOKS	1621

☒ **Claims renumbered in the same order as presented by applicant** ☐ **CPA** ☐ **T.D.** ☐ **R.1.47**

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original
	1		17		33										
	2		18		34										
	3		19		35										
	4		20		36										
	5		21		37										
	6		22		38										
	7		23		39										
	8		24		40										
	9		25		41										
	10		26		42										
	11		27		43										
	12		28		44										
	13		29		45										
	14		30		46										
	15		31												
	16		32												

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	46	
/CLINTON BROOKS/ Primary Examiner.Art Unit 1621	12/8/2013	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	NONE

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13229016	BEKTESEVIC ET AL.
	Examiner	Art Unit
	CLINTON BROOKS	1621

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	06/03/2013	12/08/2013							
1	1	=	=							
2	2	=	=							
3	3	=	=							
4	4	=	=							
5	5	=	=							
6	6	=	=							
7	7	=	=							
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9	9	=	=							
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32	32	=	=							
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34	34	=	=							
35	35	=	=							
36	36	=	=							

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13229016	BEKTESEVIC ET AL.
	Examiner	Art Unit
	CLINTON BROOKS	1621

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
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37	37	=	=							
38	38	=	=							
39	39	=	=							
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42	42	=	=							
43	43	=	=							
44	44	=	=							
45	45	=	=							
46	46	=	=							

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	13229016	BEKTESEVIC ET AL.
	Examiner	Art Unit
	CLINTON BROOKS	1621

CPC- SEARCHED		
Symbol	Date	Examiner

CPC COMBINATION SETS - SEARCHED		
Symbol	Date	Examiner

US CLASSIFICATION SEARCHED			
Class	Subclass	Date	Examiner

SEARCH NOTES		
Search Notes	Date	Examiner
Searched EAST (keyword, inventor names, ids; USPAT, USPGPUB, EPO, JPO, DERWEENT)	6/3/2013	
Searched STN (keyword, inventor names, registry nos; CAPLUS, REGISTRY)	6/3/2013	/CB/
Searched PALM (inventor names)	6/3/2013	/CB/
Searched EAST (keyword, inventor names, ids; USPAT, USPGPUB, EPO, JPO, DERWEENT)	12/8/2013	/CB/

INTERFERENCE SEARCH			
US Class/ CPC Symbol	US Subclass / CPC Group	Date	Examiner
	Performed Interference Search (UPAT, UPAD)	12/8/2013	/CB/

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: **Selma Bektesevic, et al.** Examiner: **Clinton A. Brooks**

Application No.: **13/229,016** Conf. No. **8706** Group Art Unit: **1671**

Filed: **September 9, 2011** Attorney Docket No. **H0024680**

Title: **INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS**

FILED ELECTRONICALLY

Mail Stop: Amendments
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

AMENDMENT PURSUANT TO 37 C.F.R. 1.312

Madam:

This Amendment is being filed to amend the specification under 37 C.F.R. 1.312. Applicants believe that no fees are due in connection with filing this amendment. If any fees are necessary in order to continue the prosecution of this application, please charge such fees to Deposit Account 50-1943.

Amendments to the Specification begin on page 2.

Remarks begin on page 3.

AMENDMENT TO THE SPECIFICATION

Kindly amend the Cross Reference To Related Applications section beginning on page 1, as follows:

-- CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is related to and claims the priority benefit of United States provisional application number 61/392,242, filed October 12, 2010, the contents of which are incorporated herein by reference.

[0002] This application is also a continuation-in-part of United States application serial number 13/195,429, filed August 1, 2011 (now U.S. Patent No. 8,242,316), which is a continuation of U.S. Patent Application No. 12/402,372, filed March 11, 2009 (now U.S. Patent No. 8,013,194), which in turn claims priority benefit of US Provisional Patent Application No. 61/036,526, filed March 14, 2008, each of which is incorporated herein by reference.--

REMARKS

This application has been allowed. The Cross References to Related Applications section of the specification is being amended to properly reflect the status of each related application. An updated Application Data Sheet is also being filed concurrently herewith. Support for this amendment may be found on the Bibliographic Data Sheet issued by the USPTO on June 6, 2013. No new matter has been added.

These amendments are appropriate under 37 C.F.R. 1.312 after issuance of a Notice of Allowance as they merely correct formal matters. Accordingly, Applicant respectfully requests that the Office approve and enter these amendments. The Examiner is invited to contact Applicants' undersigned representative in order to further the prosecution of this application in any way.

Respectfully submitted,

Dated: March 11, 2014

/J. Eric Sumner/

J. Eric Sumner
Registration No. 58,699
Eagleview Corporate Center
747 Constitution Drive, Suite 100
Exton, PA 19341
Tel: 610-458-6712
Fax: 610-458-7337
Email: esumner@foxrothschild.com

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	H0024680-4511
	Application Number	
Title of Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	SELMA		BEKTESEVIC	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Williamsville	State/Province	NY	Country of Residence i	US

Mailing Address of Inventor:

Address 1	770 Maple Road, Apt. 9B		
Address 2			
City	Williamsville	State/Province	NY
Postal Code	14221	Country i	US

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	HSUEH	SUNG	TUNG	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

City	Getzville	State/Province	NY	Country of Residence i	US

Mailing Address of Inventor:

Address 1	16 Vassar Drive		
Address 2			
City	Getzville	State/Province	NY
Postal Code	14068	Country i	US

Inventor 3 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	HALUK		KOPKALLI	

Residence Information (Select One) ◉ US Residency ○ Non US Residency ○ Active US Military Service

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	H0024680-4511
	Application Number	
Title of Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS	

City	Staten Island	State/Province	NY	Country of Residence i	US

Mailing Address of Inventor:

Address 1	364 Giffords Lane		
Address 2			
City	Staten Island	State/Province	NY
Postal Code	10308	Country i	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	91970		
Email Address	patentservices-us@honeywell.com	Add Email	Remove Email

Application Information:

Title of the Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS		
Attorney Docket Number	H0024680-4511	Small Entity Status Claimed	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	3	Suggested Figure for Publication (if any)	

Filing By Reference :

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country i

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	H0024680-4511
	Application Number	
Title of Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS	

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	(•) Customer Number	( ) US Patent Practitioner	( ) Limited Recognition (37 CFR 11.9)
Customer Number	91970		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this information in the application data sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the application number blank.

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
13229016	Claims benefit of provisional	61392242	2010-10-12

Prior Application Status	Patented				Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)	Patent Number	Issue Date (YYYY-MM-DD)
	Continuation in part of	13195429	2011-08-01	8242316	2012-08-14

Prior Application Status	Patented				Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)	Patent Number	Issue Date (YYYY-MM-DD)
13195429	Continuation in part of	12402372	2009-03-11	8013194	2011-09-06

Prior Application Status	Expired		Remove
Application Number	Continuity Type	Prior Application Number	Filing Date (YYYY-MM-DD)
12402372	Claims benefit of provisional	61036526	2008-03-14

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button. Add

Foreign Priority Information:

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	H0024680-4511
	Application Number	
Title of Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS	

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55(d). When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX) [i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(h)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country [i]	Filing Date (YYYY-MM-DD)	Access Code [i] (if applicable)

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button. Add

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

Authorization to Permit Access:

☒ Authorization to Permit Access to the Instant Application by the Participating Offices

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	H0024680-4511
	Application Number	
Title of Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS	

If checked, the undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the World Intellectual Property Office (WIPO), and any other intellectual property offices in which a foreign application claiming priority to the instant patent application is filed access to the instant patent application. See 37 CFR 1.14(c) and (h). This box should not be checked if the applicant does not wish the EPO, JPO, KIPO, WIPO, or other intellectual property office in which a foreign application claiming priority to the instant patent application is filed to have access to the instant patent application.

In accordance with 37 CFR 1.14(h)(3), access will be provided to a copy of the instant patent application with respect to: 1) the instant patent application-as-filed; 2) any foreign application to which the instant patent application claims priority under 35 U.S.C. 119(a)-(d) if a copy of the foreign application that satisfies the certified copy requirement of 37 CFR 1.55 has been filed in the instant patent application; and 3) any U.S. application-as-filed from which benefit is sought in the instant patent application.

In accordance with 37 CFR 1.14(c), access may be provided to information concerning the date of filing this Authorization.

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1 Remove

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

(•) Assignee	( ) Legal Representative under 35 U.S.C. 117	( ) Joint Inventor
( ) Person to whom the inventor is obligated to assign.	( ) Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor :

If the Applicant is an Organization check here. [X]

Organization Name	HONEYWELL INTERNATIONAL INC.

Mailing Address Information:

Address 1	101 Columbia Road		
Address 2			
City	Morristown	**State/Province**	NJ
Country [i]	US	Postal Code	07962
Phone Number	973-455-2062	Fax Number	973-455-5904

PTO/AIA/14 (12-13)
Approved for use through 01/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	H0024680-4511
	Application Number	
Title of Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS	

Email Address	patentservices-us@honeywell.com

Additional Applicant Data may be generated within this form by selecting the Add button. Add

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not subsitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Assignee 1

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication . An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

Remove

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Prefix	**Given Name**	Middle Name	**Family Name**	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		**State/Province**	
Country i		Postal Code	
Phone Number		Fax Number	
Email Address			

Additional Assignee or Non-Applicant Assignee Data may be generated within this form by selecting the Add button. Add

Signature:

Remove

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications

Signature	/J. Eric Sumner/			Date (YYYY-MM-DD)	2014-03-11
First Name	John	Last Name	Sumner	Registration Number	58699

Additional Signature may be generated within this form by selecting the Add button. Add

PTO/AIA/14 (12-13)
Approved for use through 01/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	H0024680-4511
	Application Number	
Title of Invention	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS	

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt

EFS ID:	18431945
Application Number:	13229016
International Application Number:	
Confirmation Number:	8706
Title of Invention:	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS
First Named Inventor/Applicant Name:	SELMA BEKTESEVIC
Customer Number:	91970
Filer:	John Eric Sumner/Mary McCrudden
Filer Authorized By:	John Eric Sumner
Attorney Docket Number:	H0024680-4511
Receipt Date:	11-MAR-2014
Filing Date:	09-SEP-2011
Time Stamp:	14:02:20
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		Rule312AmendmentH0024680.PDF	93461 d7530845c94b978a9452c534320392bf76005c21	yes	3

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Amendment after Notice of Allowance (Rule 312)	1	1
	Specification	2	2
	Applicant Arguments/Remarks Made in an Amendment	3	3

Warnings:					
Information:					
2	Application Data Sheet	SupplementalADSH00246804511.PDF	1315220 7279457d2493e1d91c944fe4134e109e1afeb94f	no	8
Warnings:					
Information:					
		Total Files Size (in bytes):	1408681		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

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.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), to: Mail **Mail Stop ISSUE FEE**
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
or Fax (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence including the Patent, advance orders and notification of maintenance fees will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications.

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

91970 7590 12/13/2013
HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission
I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being facsimile transmitted to the USPTO (571) 273-2885, on the date indicated below.

(Depositor's name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/229,016	09/09/2011	SELMA BEKTESEVIC	H0024680-4511	8706

TITLE OF INVENTION: INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$XXX 960.00	$XXX	$0	$XXXX $960.00	03/13/2014

EXAMINER	ART UNIT	CLASS-SUBCLASS
BROOKS, CLINTON A	1621	570-157000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list

(1) the names of up to 3 registered patent attorneys or agents OR, alternatively,

(2) the name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 Bruce O. Bradford
2 _____
3 _____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document has been filed for recordation as set forth in 37 CFR 3.11. Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: HONEYWELL INTERNATIONAL INC.

(B) RESIDENCE: (CITY and STATE OR COUNTRY): Morristown, NJ

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. The following fee(s) are submitted:

☐ Issue Fee
☐ Publication Fee (No small entity discount permitted)
☐ Advance Order - # of Copies _____

4b. Payment of Fee(s): **(Please first reapply any previously paid issue fee shown above)**

☐ A check is enclosed.
☒ Payment by credit card. Form PTO-2038 is attached.
☒ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment, to Deposit Account Number 50-1943 (enclose an extra copy of this form).

PTOL-85 (Rev. 02/11)

5. **Change in Entity Status** (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29	NOTE: Absent a valid certification of Micro Entity Status (see form PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.
☐ Applicant asserting small entity status. See 37 CFR 1.27	NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.
☐ Applicant changing to regular undiscounted fee status.	NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: The Issue Fee and Publication Fee (if required) will not be accepted from anyone other than the applicant; a registered attorney or agent; or the assignee or other party in interest as shown by the records of the United States Patent and Trademark Office.

Authorized Signature /J. Eric Sumner/ Date March 13, 2014

Typed or printed name J. Eric Sumner Registration No. 58,699

This collection of information is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450.

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Electronic Patent Application Fee Transmittal

Application Number:	13229016
Filing Date:	09-Sep-2011
Title of Invention:	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS
First Named Inventor/Applicant Name:	SELMA BEKTESEVIC
Filer:	John Eric Sumner/Patricia Frisoli
Attorney Docket Number:	H0024680-4511

Filed as Large Entity

Utility under 35 USC 111(a) Filing Fees

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Utility Appl Issue Fee	1501	1	960	960
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
			Total in USD ($)	**960**

Electronic Acknowledgement Receipt

EFS ID:	18459889
Application Number:	13229016
International Application Number:	
Confirmation Number:	8706
Title of Invention:	INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS
First Named Inventor/Applicant Name:	SELMA BEKTESEVIC
Customer Number:	91970
Filer:	John Eric Sumner/Patricia Frisoli
Filer Authorized By:	John Eric Sumner
Attorney Docket Number:	H0024680-4511
Receipt Date:	13-MAR-2014
Filing Date:	09-SEP-2011
Time Stamp:	14:18:31
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	Credit Card
Payment was successfully received in RAM	$960
RAM confirmation Number	647
Deposit Account	501943
Authorized User	SUMNER, JOHN ERIC

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

Charge any Additional Fees required under 37 C.F.R. Section 1.17 (Patent application and reexamination processing fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.19 (Document supply fees)

Charge any Additional Fees required under 37 C.F.R. Section 1.20 (Post Issuance fees)

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	Issue Fee Payment (PTO-85B)	Issuefeetransmittal.PDF	135661 045d6cfcf46045376bf8317b710663ae614e4887	no	2
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	30513 6d036869dc452474f19eacf62326697f0ee8e12d	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	166174		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

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.

OK TO ENTER: /C.B./

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: **Selma Bektesevic, et al.** Examiner: **Clinton A. Brooks**

Application No.: **13/229,016** Conf. No. **8706** Group Art Unit: **1671**

Filed: **September 9, 2011** Attorney Docket No. **H0024680**

Title: **INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS**

FILED ELECTRONICALLY

Mail Stop: Amendments
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

AMENDMENT PURSUANT TO 37 C.F.R. 1.312

Madam:

This Amendment is being filed to amend the specification under 37 C.F.R. 1.312. Applicants believe that no fees are due in connection with filing this amendment. If any fees are necessary in order to continue the prosecution of this application, please charge such fees to Deposit Account 50-1943.

Amendments to the Specification begin on page 2.

Remarks begin on page 3.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
13/229,016	04/29/2014	8710282	H0024680-4511	8706

91970 7590 04/09/2014

HONEYWELL/FOX ROTHSCHILD
Patent Services
101 Columbia Road
Morristown, NJ 07962

ISSUE NOTIFICATION

The projected patent number and issue date are specified above.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 19 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Application Information Retrieval (PAIR) WEB site (http://pair.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Data Management (ODM) at (571)-272-4200.

APPLICANT(s) (Please see PAIR WEB site http://pair.uspto.gov for additional applicants):

SELMA BEKTESEVIC, Williamsville, NY;
HSUEH SUNG TUNG, Getzville, NY;
HALUK KOPKALLI, Staten Island, NY;

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The USA offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to encourage and facilitate business investment. To learn more about why the USA is the best country in the world to develop technology, manufacture products, and grow your business, visit SelectUSA.gov.