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(71) Applicant: **HONEYWELL INTERNATIONAL INC.** [US/US]; Patent Services M/S AB/2B, 101 Columbia Road, P.O. Box 2245, Morristown, New Jersey 07962-2245 (US).

(72) Inventors: **BEKTESEVIC, Selma**; Honeywell International Inc., Patent Services M/S AB/2B, 101 Columbia Road, P.O. Box 2245, Morristown, New Jersey 07962-2245 (US). **WANG, Haiyou**; Honeywell International Inc., Patent Services M/S AB/2B, 101 Columbia Road, P.O. Box 2245, Morristown, New Jersey 07962-2245 (US). **TUNG, Hsueh Sung**; Honeywell International Inc., Patent Services M/S AB/2B, 101 Columbia Road, P.O. Box 2245, Morristown, New Jersey 07962-2245 (US).

(74) Agent: **BEATUS, Carrie**; Honeywell International Inc., Patent Services M/S AB/2B, 101 Columbia Road, P.O. Box 2245, Morristown, New Jersey 07962-2245 (US).

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(54) Title: METHODS OF HANDLING CHLORINATED COMPOUNDS USED FOR MANUFACTURING HFO-1234YF

(57) Abstract: This invention provides methods for handling, storing and/or transporting reactive chlorinated compounds such as 1230xa whereby decomposition reactions are reduced or eliminated by employing one or more anti-decomposition techniques selected from the group consisting of: (a) providing a 1230xa supply with little or no moisture, HCl, and/or metallic ions, (b) providing a storage and/or transport tank preferably lined and/or coated with one or more suitable materials, (c) transferring 1230xa, preferably stabilized 1230xa, into a storage and/or transportation tank in such a way that no exposure of the 1230xa to air occurs, (d) handling, storing, and/or transporting 1230xa under the protection of a dried inert gas such as nitrogen, (e) optionally providing a device that can remove any HCl generated during the storage and/or transportation of 1230xa; and (f) combinations of two or more of these anti-decomposition techniques.

METHODS OF HANDLING CHLORINATED COMPOUNDS USED FOR MANUFACTURING HFO-1234yf

CROSS-REFERENCE TO RELATED APPLICATION

This application claims benefit of U.S. Provisional Patent Application Serial No. 61/760,332 filed February 4, 2012, the disclosure of which is hereby incorporated herein by reference.

BACKGROUND OF THE INVENTION

The compound 2,3,3,3-tetrafluoropropene (HFO-1234yf) is a low GWP molecule, which can be used as refrigerant, blowing agent, cleaning agent, as well as a monomer of macromolecule compounds. As disclosed in U.S. Patent No. 8,058,486, a manufacturing process for 1234yf that uses one of three chlorinated compounds, namely, 1,1,2,3-tetrachloropropene (1230xa), 2,3,3,3-tetrachloropropene (1230xf), and 1,1,1,2,3-pentachloropropane (240db) as starting raw material, includes the following three steps:

1) 1230xa (or 1230xf or 240db) + HF --> 1233xf + HCl in a vapor phase reactor charged with a solid catalyst,
2) 1232xf + HF --> 244bb in a liquid phase reactor charged with a liquid catalyst,

and

3) 244bb --> l234yf in a vapor phase reactor.

These feed materials are usually stored in containers made from plastic, carbon steel, and/or stainless steel. Chlorinated compounds such as 1230xa, 1230xf, and 240db, are known to decompose under certain conditions. Those conditions include the presence of air (oxygen), moisture and metal components. While not wishing to be bound to any theory, the present inventors believe that 1230xa, 1230xf, and 240db decomposition occurs due to one or more of the following factors:

(i) atmospheric oxidation of these chlorinated compounds occurs in the presence of oxygen (e.g., included in air), resulting in the formation of phosgenes;

(ii) hydrolysis of these chlorinated compounds takes place in the presence of moisture, resulting in the formation of HCl and organic compound(s);

(iii) dehydrochlorination of these chlorinated compounds might occur in the presence of metallic salts, resulting in the formation of HCl and organic compound; and

(iv) dimerization of these chlorinated compounds might take place in the presence of metal components, resulting in the formation of dimers (or oligomers) and metallic chlorides.

The detrimental impacts resulting from these potential decomposition reactions include purity drop due to the conversion of these chlorinated compounds to other organic compounds and accelerated corrosion of storage containers due to HCl formation. Thus, there is a continuing need for means by which these chlorinated compounds can be suitably handled, stored and/or transported, wherein little or no degradation or decomposition occurs.

SUMMARY OF THE INVENTION

The solution to the decomposition problem of chlorinated compounds including 1230xa, 1230xf and/or 240db as detailed herein comprises the implementation of one or more of the following anti-decomposition techniques which reduce and/or prevent the decomposition of these chlorinated compounds and similar chlorinated compounds that decompose under similar conditions. In certain embodiments, two or more, preferably three or more, and more preferably, all of these techniques are employed. While 1230xa is specifically mentioned below, other chlorinated compounds such as 1230xf, 1230za, trans-1230xd, cis-1230xd, 1240za, 1240zf, 250fb, and 240db, can also be treated in a like manner to reduce and/or prevent decomposition:

(1) provide a 1230xa feed supply with little or no moisture, HCl, and metallic ions,

(2) provide a storage and/or transport tank preferably lined and/or coated with suitable materials,

(3) transfer 1230xa, optionally stabilized 1230xa, into a storage and/or transportation tank in such a way that no exposure of 1230xa to air occurs,

(4) handle, store, and/or transport 1230xa under the protection of dried nitrogen, and

(5) optionally provide a method and/or device that can remove any HCl generated during storage and/or transportation.

It should be appreciated by those persons having ordinary skill in the art(s) to which the present invention relates that any of the features described herein in respect of any particular aspect and/or embodiment of the present invention can be combined with

one or more of any of the other features of any other aspects and/or embodiments of the present invention described herein, with modifications as appropriate to ensure compatibility of the combinations. Such combinations are considered to be part of the present invention contemplated by this disclosure.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention as claimed. Other embodiments will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein.

DETAILED DESCRIPTION OF THE INVENTION

As described above, the present invention provides methods for handling, storing and/or transporting 1230xa, and similar reactive chlorinated compounds, whereby decomposition reactions including a purity drop due to conversion to other organic compounds and accelerated corrosion of containers due to HCl formation are reduced or eliminated by employing one or more of the anti-decomposition techniques selected from the group consisting of: (1) providing a 1230xa supply with little or no moisture, HCl, and/or metallic ions, (2) providing a storage and/or transport tank preferably lined and/or coated with one or more suitable materials, (3) transferring 1230xa, preferably stabilized 1230xa, into a storage and/or transportation tank in such a way that no exposure of the 1230xa to air occurs, (4) handling, storing, and/or transporting 1230xa under the protection of a dried inert gas such as nitrogen, (5) optionally providing a device that can remove any HCl generated during the storage and/or transportation of 1230xa; and (6) combinations of two or more of these anti-decomposition techniques.

One embodiment of the present invention can be generally described as a method for handling, storing, and/or transporting l230xa. Step (1) above thus provides a 1230xa feed supply with little or no moisture, HCl, and/or metallic ions therein. In this 1230xa feedstock the moisture level is generally lower than 100 ppm, preferably 50 ppm, and

more preferably 25 ppm. In this 1230xa feedstock the HCl level is generally lower than 200 ppm, preferably 50 ppm, and more preferably 10 ppm. In this 1230xa feedstock the metallic ion content, e.g., iron ion content, is generally lower than 10 ppm, preferably 5 ppm, and more preferably 2 ppm. Various known methods can be used to achieve each of these values.

Any conventional technique can be used to remove moisture. Non-limiting techniques include distillation, and/or absorption using desiccants, and/or the like. Distillation can be operated at atmospheric pressure, super-atmospheric pressure or under vacuum and can be performed using standard distillation methods for separating two compounds. Another method of removing the moisture from 1230xa is by the use of desiccants, whereby the desiccant is in contact with 1230xa for sufficient amount of time to reduce the moisture content. While various desiccants can be used in a variety of ways, in certain embodiments 1230xa is dried in pre-packaged desiccant in continuous mode. Non-limiting desiccants include silica gel, activated charcoal, calcium sulfate, calcium chloride, montmorillonite clay, and various molecular sieves. The moisture content present in 1230xa is measured by conventional means, such as Karl Fischer titration and the like.

Any techniques known in the art can be used to remove HCl. In one preferred embodiment, HCl is removed by distillation. Single column or multiple columns may be used. Distillation can be operated at atmospheric pressure, super-atmospheric pressure or under vacuum and can be performed using standard distillation methods for separating two compounds. The amount of HCl present in 1230xa is determined using standard techniques known in the art. For example, the amount of HCl present is determined by acid-base titration or IC (Ion Chromatography).

Any techniques known in the art can be used to remove ionic iron. In one embodiment, it is removed by distillation. Single column or multiple columns may be used. Distillation can be operated at atmospheric pressure, super-atmospheric pressure or

under vacuum and can be performed using standard distillation methods for separating two compounds. The amount of ionic iron present in 1230xa is determined using standard techniques known in the art. For example, the amount of iron present is determined by ICP (Inductive Coupled Plasma).

Another embodiment of the present invention can be generally described as a storage and/or transport tank, preferably lined/coated with suitable non-reactive materials. Step (2) above thus provides a storage/transport tank preferably lined/coated with suitable materials, Carbon steel, stainless steel and plastic can be used to make the desired storage and/or transport tank. However, a carbon steel tank internally lined and/or coated with suitable material is preferred. Non-limiting examples of suitable lining and/or coating materials include glass, ceramic, a phenolic or epoxy resin liner such as Plasite 3070 (available from Carboline Company), Plasite 9573 (available from Carboline Company), and Phenicon HS Flake Filled (available from Sherwin Williams), and the like.

Yet another embodiment of the present invention can be generally described as a method of transfer of 1230xa such that decomposition is minimized or eliminated. Step (3) above thus provides a method for the transfer of 1230xa, optionally stabilized 1230xa into said storage/transportation tank in such a way that little or no exposure of 1230xa to air occurs. Before making any 1230xa transfer, all equipment and the storage and/or transportation tank are subject to an effective purge with a dried inert gas (e.g., nitrogen) to displace air. Optionally but preferably, 1230xa is added with a stabilizer before being transferred or transported. Non-limiting examples include, but are not limited to, diisopropylamine, triethylamine, 4-tert-Amylphenol, 4-methoxyphenol, and their combinations. The amount of stabilizer(s) present in 1230xa can range from about 1 to about 1000 ppm, preferably from about 2 to about 100 ppm, more preferably from about 3 to about 50 ppm, and most preferably from about 4 to about 20 ppm.

Another embodiment of the present invention can be generally described as a

method of protecting 1230xa such that decomposition is minimized or eliminated. Step (4) above is similar to Step (3), wherein the storage and/or transport of 1230xa takes place under the protection of an excess amount of dried nitrogen. In this embodiment, after the 1230xa is transferred into a storage and/or transportation tank, the tank is pressurized with dried nitrogen and is then sealed (closed to the atmosphere) to prevent air and/or moisture from entering the tank.

Yet another embodiment of the present invention can be generally described as a method of protecting 1230xa such that decomposition is minimized or eliminated. Step (5) above makes use of a device and/or method that is effective in removing any HCl generated during the storage and/or transportation of 1230xa. One way of removing HCl is by having either constant or periodical purge of nitrogen and/or any other inert gas through a column loaded with solid basic sorbent before venting. Non-limiting solid sorbents include, but are not limited to, alumina, calcium carbonate, sodium carbonate, sodium aluminate, and the like.

EXAMPLES

The following examples provide test data for various materials exposed to 1230xa.

Example 1

This example illustrates the effectiveness of 3A molecular sieves for removing moisture from 1230xa feed. The1230xa used in Example 1 had a purity of 99.2 GC (gas chromatogram) area% and contained 100 ppm of moisture. 5 ppm of di-isopropyl amine was added into 1230xa as a stabilizer. The 1230xa feed was passed through a 2" ID column loaded with 2 liters of 3A molecular sieves at rate of 1.0 lb/h and sample was taken from a sampling port after drying column. Moisture level was determined to be 12

ppm by using Mitsubishi Moisture Meter (Model CA-100), indicating 3A molecular sieve is an effective drying agent for 1230xa.

Example 2

Three materials were evaluated as a possible MOC (material of construction) for a shipping and/or storage container for 1230xa. The materials were carbon steel, stainless steel, and carbon steel coated with Plasite 3070. Four glass tubes were filled with the same amount of solution containing 1230xa and 5 ppm of di-isopropyl amine. Carbon steel, stainless steel, and Plasite 3070 coupons were placed into tube containing solution of 1230xa-di-isopropyl amine and the tubes were then closed. The fourth tube (blank) contained no coupon. All transfers were done under atmosphere of nitrogen. All coupons were 5" long, 1" wide, and 1/8" thick. The tubes were then transferred to an oven kept at 50°C. Periodical visual observations were made and photographs of the tubes were taken. After one week at 50°C, the 1230xa solution in the tube containing carbon steel coupon turned brown-yellow and corrosion of the carbon steel coupon was noted, indicating the occurrence of chemical reactions such as breakdown of 1230xa. After 4 weeks at 50°C, the 1230xa solution in the tube containing stainless steel coupon was pale yellow, however, no corrosion of the stainless steel coupon was noted. After 90 days at 50°C, the 1230xa solution in the tube containing Plasite 3070 coupon remained as clear visually as the blank sample. These results indicate that stainless steel can be a suitable MOC for vessels for transporting 1230xa and that Plasite 3070 can serve as a liner or coating for 1230xa storage tanks.

As used herein, the singular forms "a", "an" and "the" include plural unless the context clearly dictates otherwise. Moreover, when an amount, concentration, or other value or parameter is given as either a range, preferred range, or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed.

Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

It should be understood that the foregoing description is only illustrative of the present invention. Various alternatives and modifications can be devised by those skilled in the art without departing from the invention. Accordingly, the present invention is intended to embrace all such alternatives, modifications and variances that fall within the scope of the appended claims.

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WHAT IS CLAIMED IS:

1. A method for handling, storing and/or transporting reactive chlorinated compounds selected from the group consisting of 1230xa, 1230xf, 1230za, trans-1230xd, cis-1230xd, 1240za, 1240zf, 250fb, and 240db, whereby decomposition reactions including a purity drop due to conversion of the reactive compounds to other organic compounds and accelerated corrosion of containers due to HCl formation are reduced or eliminated by employing one or more anti-decomposition techniques selected from the following:

(a) providing a reactive compound supply with little or no moisture, HCl, and/or metallic ions,

(b) providing a storage and/or transport tank preferably lined and/or coated with one or more suitable materials,

(c) transferring the reactive compounds into a storage and/or transportation tank in such a way that no exposure of the compounds to air occurs,

(d) handling, storing, and/or transporting the reactive compounds under the protection of a dried inert gas,

(e) optionally providing a device that can remove any HCl generated during the storage and/or transportation of the reactive compounds; and

(f) combinations of two or more of these anti-decomposition techniques.

2. The method of Claim 1, wherein the reactive compound is selected from the following; 1230xa; 1230xf; and 240db.

3. The method of Claim 2, wherein the supply of the reactive compound includes a moisture level lower than 100 ppm.

4. The method of Claim 2, wherein the supply of the reactive compound includes a moisture level lower than 50 ppm.

5. The method of Claim 2, wherein the supply of the reactive compound includes a moisture level lower than 25 ppm.

6. The method of Claim 2, wherein the supply of the reactive compound includes an HCl level lower than 200 ppm.

7. The method of Claim 2, wherein the supply of the reactive compound includes an HCl level lower than 100 ppm.

8. The method of Claim 2, wherein the supply of the reactive compound includes an HCl level lower than 50 ppm.

9. The method of Claim 2, wherein the supply of the reactive compound includes a metallic ion content lower than 10 ppm.

10. The method of Claim 2, wherein the supply of the reactive compound includes a metallic ion content lower than 5 ppm.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/013742

A. CLASSIFICATION OF SUBJECT MATTER

C01B 7/03(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)
C01B 7/03; C07C 17/10; C07C 17/25; C07C 21/18; C07H 5/02; C07C 21/04; C07C 17/087; C07C 17/386; C07C 17/278; B01J 19/00; C07H 1/06

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: chlorinated compounds, anti-decomposition, moisture, HCl, metallic ions, air, distillation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011-060211 A1 (ARKEMA INC.) 19 May 2011 See abstract; claims 1, 4, 6; and page 3, line 5-page 4, line 27.	1-10
A	US 2012-0157723 A1 (FUKUJU, T. et al.) 21 June 2012 See abstract; and paragraphs [0002], [0003], [0011], [0058], [0062]-[0064].	1-10
A	JP 2012-041289 A (TOKUYAMA CORP.) 01 March 2012 See abstract; and paragraphs [0033]-[0045].	1-10
A	US 2013-0012743 A1 (WILSON, R. L. et al.) 10 January 2013 See abstract; claims 1, 5, 6; and paragraph [0075].	1-10
A	US 2012-0178977 A1 (MERKEL, D. C. et al.) 12 July 2012 See abstract; and claims 1, 2, 5-7.	1-10
A	WO 2005-090374 A1 (PHARMED MEDICARE PRIVATE LIMITED) 29 September 2005 See abstract; and claim 1.	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 application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

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Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
SHIN, Ju Cheol
Telephone No. +82-42-481-8656

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2014/013742

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011-060211 A1	19/05/2011	CN 102639475 A	15/08/2012
		EP 2501666 A1	26/09/2012
		EP 2501666 A4	26/06/2013
		JP 2013-510869 A	28/03/2013
		US 2012-0226081 A1	06/09/2012
US 2012-0157723 A1	21/06/2012	CN 102177116 A	07/09/2011
		EP 2447238 A1	02/05/2012
		EP 2447238 A4	19/12/2012
		EP 2463261 A2	13/06/2012
		EP 2463261 A3	19/12/2012
		JP 04855550 B2	18/01/2012
		JP 2012-036190 A	23/02/2012
		US 2012-0053374 A1	01/03/2012
		US 8304589 B2	06/11/2012
		WO 2010-150835 A1	29/12/2010
JP 2012-041289 A	01/03/2012	None	
US 2013-0012743 A1	10/01/2013	CA 2708643 A1	09/07/2009
		CN 101903312 A	01/12/2010
		EP 2231565 A1	29/09/2010
		EP 2687504 A2	22/01/2014
		JP 2011-507877 A	10/03/2011
		TW 200936538 A	01/09/2009
		US 2009-216055 A1	27/08/2009
		US 2012-035402 A1	09/02/2012
		US 8115038 B2	14/02/2012
		US 8487146 B2	16/07/2013
		US 8614363 B2	24/12/2013
		WO 2009-085862 A1	09/07/2009
US 2012-0178977 A1	12/07/2012	CN 103415496 A	27/11/2013
		EP 2661420 A2	13/11/2013
		KR 10-2013-0132576 A	04/12/2013
		MX 2013007782 A	12/08/2013
		WO 2012-094477 A2	12/07/2012
		WO 2012-094477 A3	10/01/2013
WO 2005-090374 A1	29/09/2005	AT 508136 T	15/05/2011
		AU 2004-317336 A1	29/09/2005
		CA 2560284 A1	29/09/2005
		CN 1946731 A	11/04/2007
		DE 602004032578 D1	16/06/2011
		EA 200601742 A1	27/02/2007
		EP 1735327 A1	27/12/2006
		EP 1735327 B1	04/05/2011
		IL 178046 D0	31/12/2006
		JP 2007-529505 A	25/10/2007

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2014/013742

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		KR 10-2008-0043194 A	16/05/2008
		LV 13585 B	20/11/2007
		MX PA06010665 A	28/03/2007
		NZ 550064 A	25/06/2010
		US 2009-0324513 A1	31/12/2009
		WO 2005-090374 A8	06/03/2008
		WO 2005-090376 A1	29/09/2005