Petitioner's Demonstratives

ARKEMA FRANCE,
Petitioner,
v.
HONEYWELL INTERNATIONAL INC.,
Patent Owner.

IPR2015-00915
IPR2015-00916
IPR2015-00917

Patent 8,710,282 B2

Claim Construction

Claim 21

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.

’282 Patent, claim 21

Claim 21 (PO's construction)

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~~ an aqueous solution containing DHA or KOH ***and by-product salts***; and

(c) recovering ~~spent KOH~~ an aqueous solution containing DHA or KOH ***and by-product salts***.

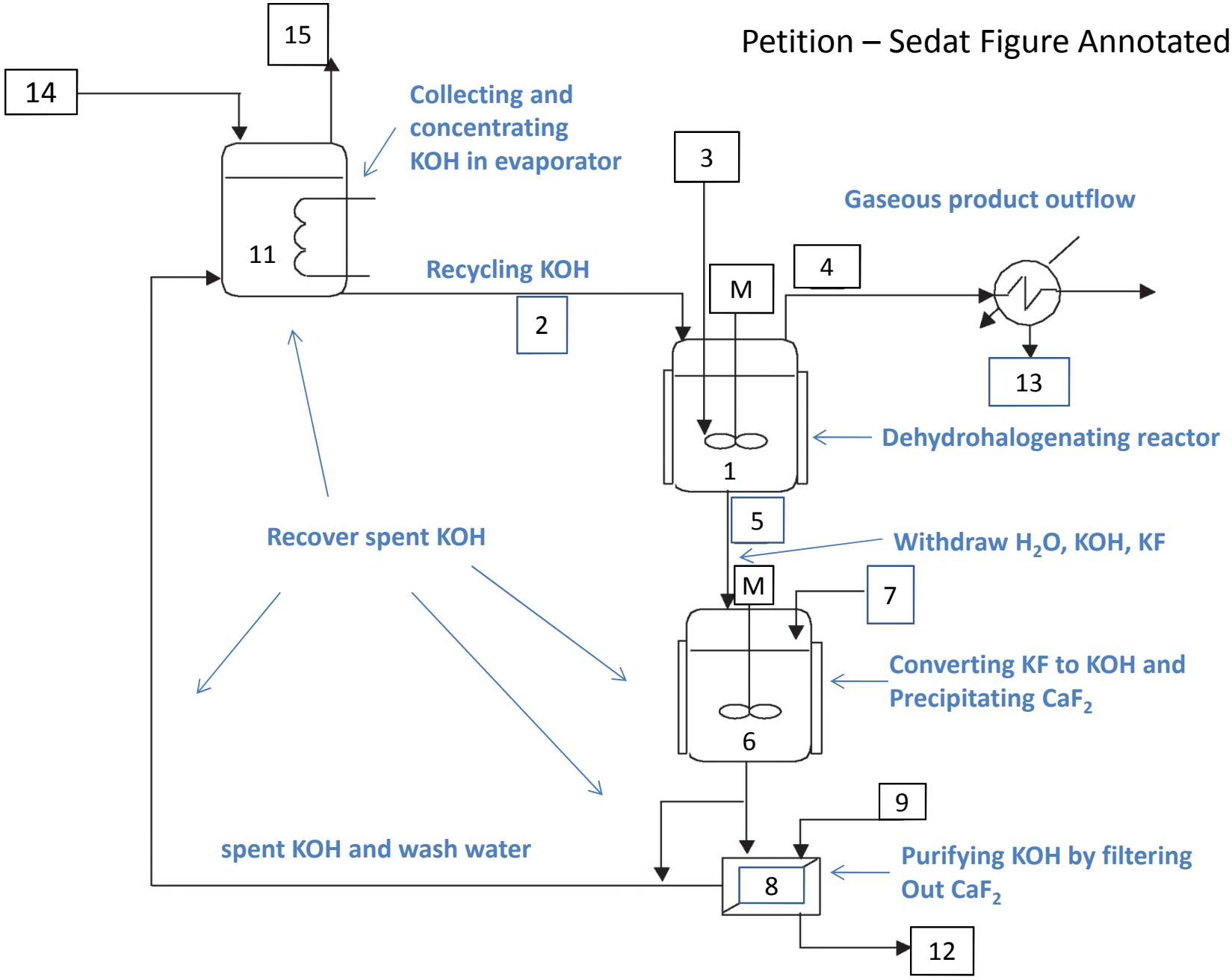
'282 Patent, claim 21 and -915 Response at 4-6

Intrinsic Record Does Not Support PO Construction of "Spent DHA/KOH"

- Specification
  - "…(d) withdrawing a reaction stream comprising **spent [DHA]** and, optionally, metal fluoride **salt by products**…". Ex.1001 at 3:13-15.
  - "[**s]pent [DHA]** and **by-product salts** (e.g., metal fluoride salts) may be withdrawn from the reactor by a product stream either continuously or intermittently using one or more separation techniques". Ex.1001 at 13:16-19.
  - "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." Ex. 1001 at 5:30-34.
- Claims
  - Claim 16 - "wherein the reaction stream further comprises by-product salts of the dehydrohalogenating agent"
  - Claims 33 and 44 - "…wherein the reaction stream further comprises KF".

'282 Patent, -915 Petition at 11-12

Petition – Sedat Figure Annotated



-915 Petition at 19

Claim Construction Comparison

* Petitioner does not dispute the claim constructions set forth in Patent Owner's Response under the broadest reasonable constructions (BRC) for the terms highlighted in **green** in the table below. For the terms "spent DHA/KOH," "dissolved organics," and "withdrawing" (highlighted in **red**), Petitioner's proposed construction is the BRC and should be used.

Claim Term	Petition Claim Construction	PO Response Claim Construction
Spent DHA/KOH	unreacted DHA or KOH remaining after the dehydrohalogenation reaction	an aqueous solution containing DHA or KOH and by-product salts
Recovering Spent DHA	collecting spent DHA or KOH, respectively, for further use (may include separating, purifying, concentrating and/or regenerating)	substantially separating spent DHA or KOH from any other materials in the [product reaction stream (Claim 1)/second product stream (Claim 10)/reaction stream (Claims 21 and 36)]
Product Reaction Stream, Second Product Stream, or Reaction Stream	a volume of material including spent DHA that may also contain by-product salts and dissolved organics	continuous flow of a fluid consisting of at least spent DHA or KOH resulting from a dehydrofluorination reaction

-915 Petition at 10-11; -915 Response at 4-12

Claim Construction Comparison (cont.)

Claim Term	Petition Claim Construction	PO Response Claim Construction
Dissolved Organics	organic that is dissolved in a stream	unreacted organic materials entrained in an aqueous solution
Withdrawing	taking out or removing	
Purifying/Purified		further separating recovered spent DHA or KOH from all other materials in the [second product stream (Claim 10)/reaction stream (Claims 21 and 36)]
Recycling	returning a component of the process to the process	returning a component of the reaction back to the reaction
Dehydrofluorinated Product Stream or Product Stream	a volume of material resulting from dehydrofluorination including dehydrofluorinated organic product(s)	continuous flow of a fluid consisting of at least the olefin products resulting from a dehydrofluorination reaction.

-915 Petition at 10-11; -915 Response at 4-12

Claim 1 requires:

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):

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

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

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

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;

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.

’282 Patent, claim 1

Claim 10 requires:

10. 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.

'282 Patent, claim 10

Claim 36 requires:

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-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.

’282 Patent, claim 36

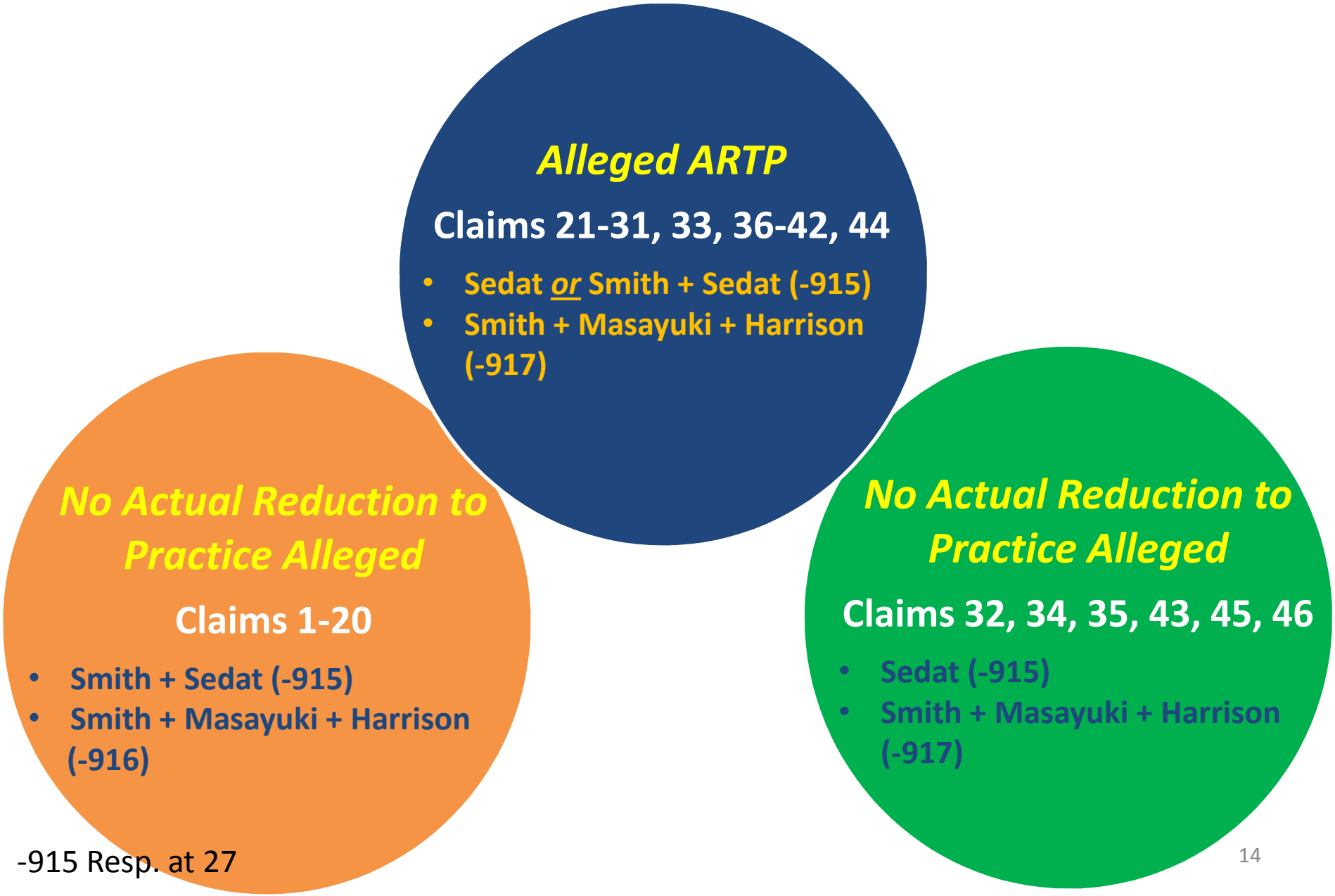
Antedating

Sedat and Smith are Prior Art

- Patent Owner failed to show actual reduction to practice for claims 21-31, 33, 36-42, 44
  - Failed under any construction (from Response and Petition)
  - Failure to perform “recovering” step of claimed process
  - Failure to determine invention worked for its intended purpose (recovering and recycling)
- Patent Owner failed to exercise diligence for claims 1-46
  - 3-month period for Sedat
  - 17-month period for Smith
- Patent Owner concealed invention for more than 2 years

-915 Reply at 12-29

Claims for which PO Alleges ARTP



-915 Resp. at 27

Claims 21 & 36

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.

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-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.

’282 Patent, claims 21 & 36

Standard to Show ARTP

- In order to establish an actual reduction to practice, a party must establish three things:

  (1) construction of an embodiment or performance of a process that meets all of the limitations of the relevant patent claim;

  (2) determination that the invention would work for its intended purpose; and

  (3) the existence of sufficient evidence to corroborate inventor testimony regarding these events.

- *Medichem, S.A. v. Rolabo, S.L.*, 437 F.3d 1157, 1169 (Fed. Cir. 2006); *see also Slip Track Sys., Inc. v. Metal-Lite, Inc.*, 304 F.3d 1256, 1263 (Fed. Cir. 2002).

Standard for "Intended Purpose"

- To show actual reduction to practice, a party "must demonstrate that the invention is suitable for its intended purpose. . . . When testing is necessary to show proof of actual reduction to practice, the embodiment relied upon as evidence of priority must actually work for its intended purpose." *Scott v. Finney*, 34 F.3d 1058, 1061 (Fed. Cir. 1994).
- "[P]roof of actual reduction to practice requires a showing that 'the embodiment relied upon as evidence of priority actually worked for its intended purpose' . . . This is so even if the 'intended purpose' is not explicitly set forth in the [claims]." *DSL Dynamic Sci. Ltd. v. Union Switch & Signal, Inc.*, 928 F.2d 1122, 1125 (Fed. Cir. 1991)
- For example, in *Tyco Healthcare Grp. LP v. Ethicon Endo-Surgery, Inc.*, 514 F. Supp. 2d 351, 360 (D. Conn. 2007), the court used patent abstracts to identify the intended purpose of the invention despite claims not reciting the intended purpose.

Intended Purpose: to Recover and Recycle

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

Abstract


US008710282B2

(12) **United States Patent**
Bektesevic et al.

(10) **Patent No.: US 8,710,282 B2**
(45) **Date of Patent: Apr. 29, 2014**

(54) **INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS**

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(73) Assignee: **Honeywell International Inc.**, Morristown, NJ (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 19 days.

(21) Appl. No.: **13/229,016**

(22) Filed: **Sep. 9, 2011**

(65) **Prior Publication Data**

US 2012/0022302 A1 Jan. 26, 2012

Related U.S. Application Data

(63) Continuation-in-part of application No. 13/195,429, filed on Aug. 1, 2011, now Pat. No. 8,242,316, which is a continuation-in-part of application No. 12/402,372, filed on Mar. 11, 2009, now Pat. No. 8,013,194.

(60) Provisional application No. 61/392,242, filed on Oct. 12, 2010, provisional application No. 61/036,526, filed on Mar. 14, 2008.

(51) **Int. Cl.**
C07C 17/25 (2006.01)
C07C 19/08 (2006.01)
C07C 21/18 (2006.01)

(52) **U.S. Cl.**
USPC **570/157**; 570/155

(58) **Field of Classification Search**
None
See application file for complete search history.

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(74) *Attorney, Agent, or Firm* — Druce O. Bradford

(57) **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.

46 Claims, 3 Drawing Sheets

Pet'rs Exhibit 1001
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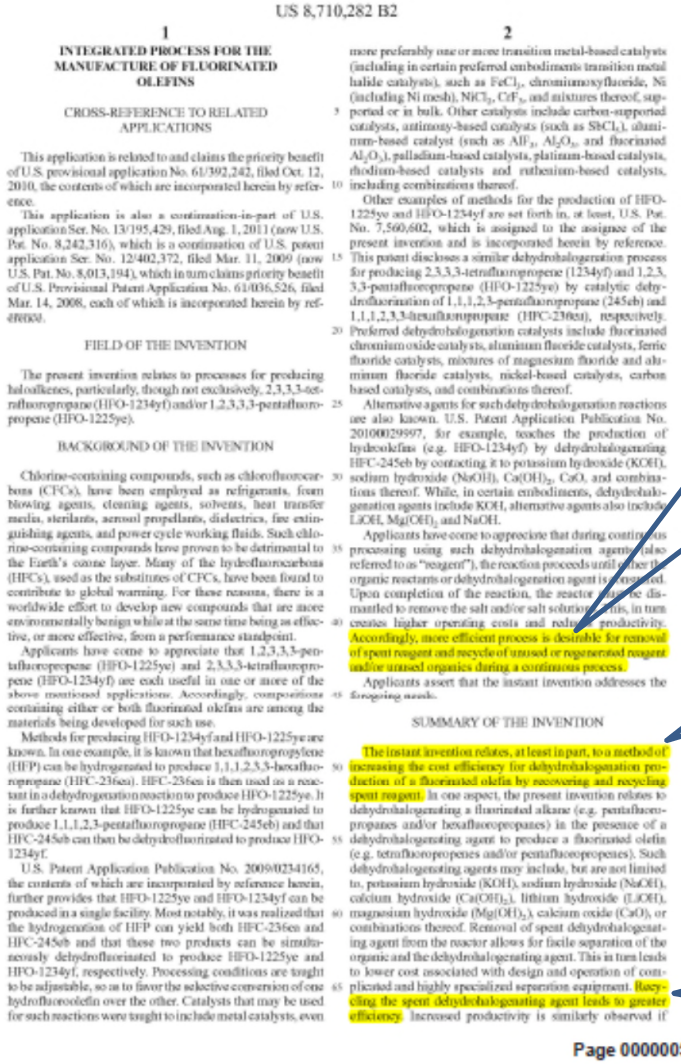
'282 Patent at 1, Abstract; -915 Reply at 16.

Exhibit 1042-00018

Intended Purpose: to Recover and Recycle



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INTEGRATED PROCESS FOR THE MANUFACTURE OF FLUORINATED OLEFINS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is related to and claims the priority benefit of U.S. provisional application No. 61/392,242, filed Oct. 12, 2010, the contents of which are incorporated herein by reference.

This application is also a continuation-in-part of U.S. application Ser. No. 13/195,429, filed Aug. 1, 2011 (now U.S. Pat. No. 8,242,316), which is a continuation of U.S. patent application Ser. No. 12/402,372, filed Mar. 11, 2009 (now U.S. Pat. No. 8,013,194), which in turn claims priority benefit of U.S. Provisional Patent Application No. 61/036,526, filed Mar. 14, 2008, each of which is incorporated herein by reference.

FIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

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.

Applicants have come to appreciate that 1,2,3,3,3-pentafluoropropene (HFO-1225ye) and 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.

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.

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

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more preferably one or more transition metal-based catalysts (including in certain preferred embodiments transition metal halide catalysts), such as $FeCl_3$, chromium oxyfluoride, 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.

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 1,2,3,3,3-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.

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.

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 solution. This, in turn creates higher operating costs and reduced 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.

Applicants assert that the instant invention addresses the foregoing needs.

SUMMARY OF THE INVENTION

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

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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.

Col. 2, lines 41-43

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

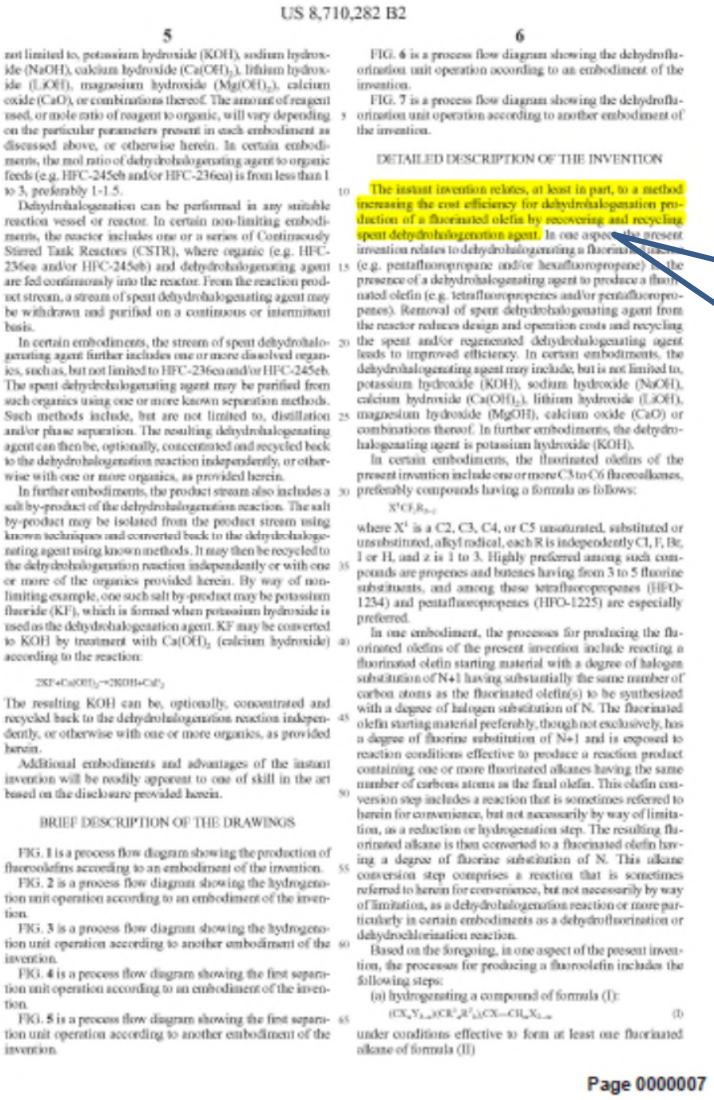
Col. 2, lines 49-52

plicated and highly specialized separation equipment. Recycling the spent dehydrohalogenating agent leads to greater efficiency. Increased productivity is similarly observed if

Col. 2, lines 65-67

'282 Patent, cols. 1 & 2; -915 Reply at 16.

Intended Purpose: to Recover and Recycle



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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.

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.

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.

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.

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

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

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

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

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

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

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

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

DETAILED DESCRIPTION OF THE INVENTION

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 [illegible] (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).

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

$$X^1CF_zR_{5-z}$$

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.

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.

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):

$$(CX_nY_{3-n})(CR^1_mR^2_{3-m})CX=CH_pX_{1-p} \quad (I)$$

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

Page 0000007

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

Col. 6, lines 10-13

'282 Patent, col. 6; -915 Reply at 16.

No Determination Invention Would Work for Intended Purpose

May 2009 Apollo Presentation:

- Issues with CSTR: Large quantity of unreacted KOH wasted.
- Possible solutions – recycle KOH.
  - Use Ca(OH)2 => solubility low; process practiced in [another project]; need more information.
  - Use NaOH instead of KOH => Conversion lower in NaOH (24 with NaOH vs. 79% with KOH)

Ex. 2028 at 5; -915 Reply at 16.

Standard to Show ARTP

- In order to establish an actual reduction to practice, a party must establish three things:

  (1) construction of an embodiment or performance of a process that meets all of the limitations of the relevant patent claim;

  (2) determination that the invention would work for its intended purpose; and

  (3) the existence of sufficient evidence to corroborate inventor testimony regarding these events.

- *Medichem, S.A. v. Rolabo, S.L.*, 437 F.3d 1157, 1169 (Fed. Cir. 2006); *see also Slip Track Sys., Inc. v. Metal-Lite, Inc.*, 304 F.3d 1256, 1263 (Fed. Cir. 2002).

Claim 21

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.

’282 Patent, claim 21

Claim 21 (PO's Construction)

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) substantially separating spent KOH from any other materials in the reaction stream.

-915 Response at 9.

Claim 21 (PO's Construction)

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) substantially separating spent KOH from any other materials in the continuous flow of a fluid consisting of at least spent KOH resulting from a dehydrofluorination reaction.

-915 Response at 10-11.

“Recovering Spent KOH”

- “. . . a POSITA would understand that a stream implies a measure of volume per unit of time, and thus, a flow of material such as a liquid or gas . . .” (PO’s -915 Response at 10).
- “From the reaction product stream, a stream of spent dehydrohalogenating agent may be withdrawn and purified on a continuous or intermittent basis.” (‘282 Pat. at 5:16-19).
- “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.” (‘282 Pat. at 13:4-6).

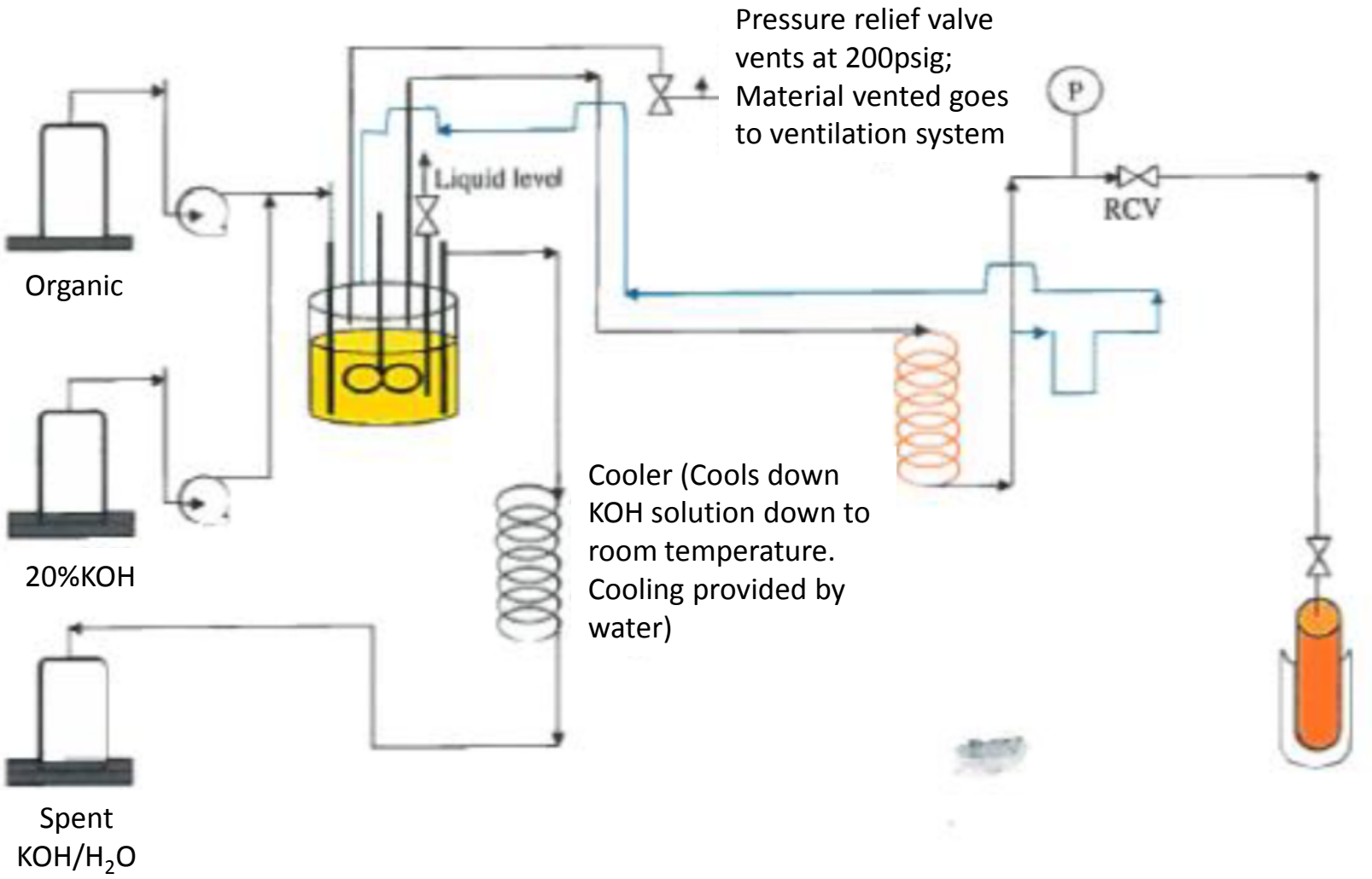
-915 Response at 10; ’282 Patent at 5:16-19, 13:4-6.

PO Cites to SPCC for ARTP of "Recovering"

Claim	Evidentiary Support
[21] (c) recovering spent KOH.	Appendix 3 illustrates the recovery of spent KOH in a **scrubber PCC [Product Collection Cylinder]**. (EX2010 at Appendix 3.) Appendices 1, 3 and 5 illustrate the recovery of spent KOH in a **scrubber PCC**. (EX2013 at Appendices 1, 3 and 5.) "Spent KOH was collected in **scrubber PCC (SPCC)**. SPCC was **pre-filled with methylene chloride** (the target was to have 15-20 wt% of MeCl2 in the final spent KOH-MeCl2 solution). Analysis of methylene chloride layer revealed that ~70 GC area % was 236ea. There was small amount of 1225ye (~2%) while the rest were some unknown heavies. In order to confirm that all organic was extracted with MeCl2, part KOH was added to part MeCl2 (i.e. 1:1). GC analysis revealed that amount of organic was negligible." (EX2016 at 2; *see also id.* at Appendix 1.)

Ex. 2002 at 53.

SPCC Failed to Perform Claimed "Recovering" Step



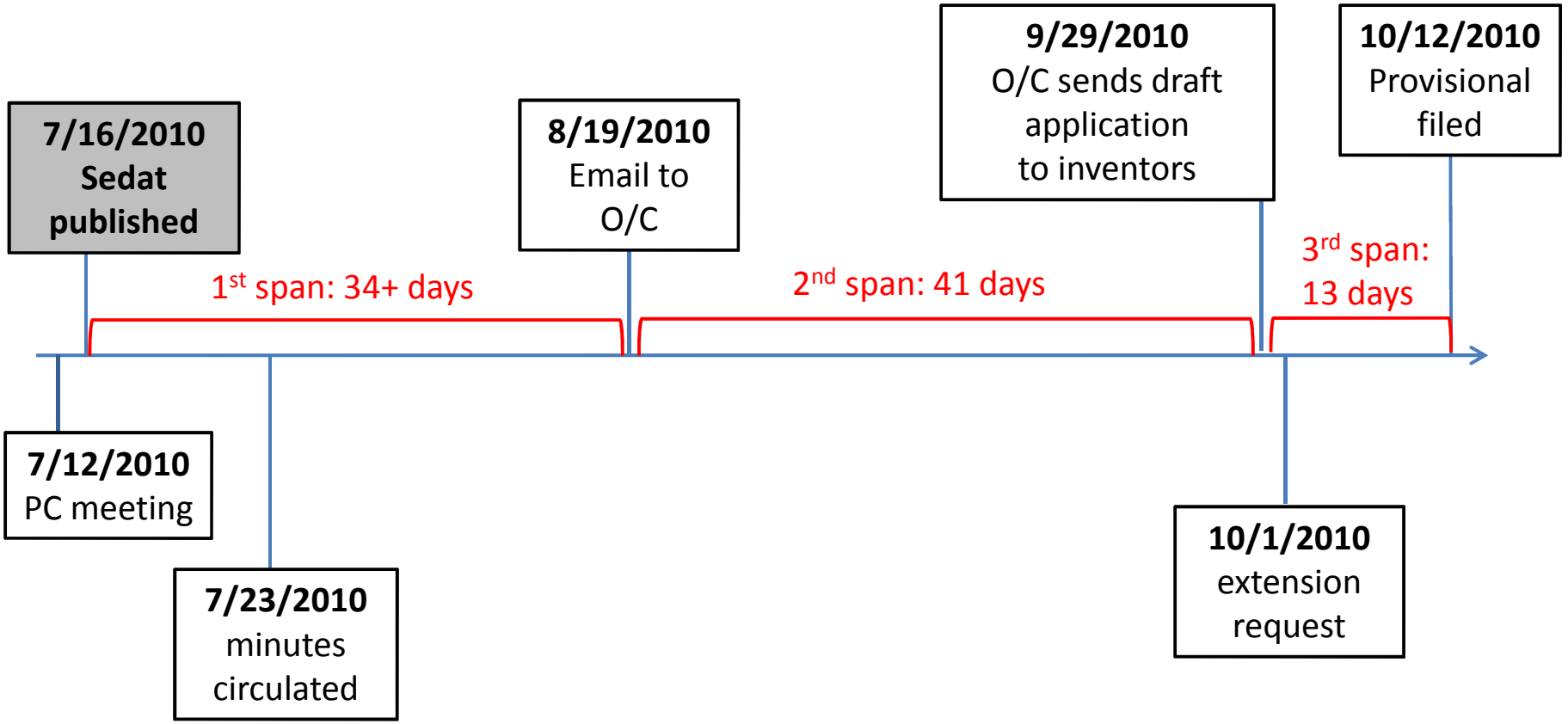
Ex. 2006 at 8; Ex. 2009 at 6; -915 Reply at 13.

Patent Owner Was Not Diligent

- Patent Owner failed to exercise diligence for claims 1-46
  - 3-month period for Sedat
  - 17-month period for Smith
- *Olympus Am. Inc. v. Perfect Surg. Tech., Inc.*, IPR2014-00233, Paper 56 at 16, 21-22 (PTAB June 8, 2015)
  - Finding lack of diligence during each of 19-day, 3-day, and 18-day spans during critical period

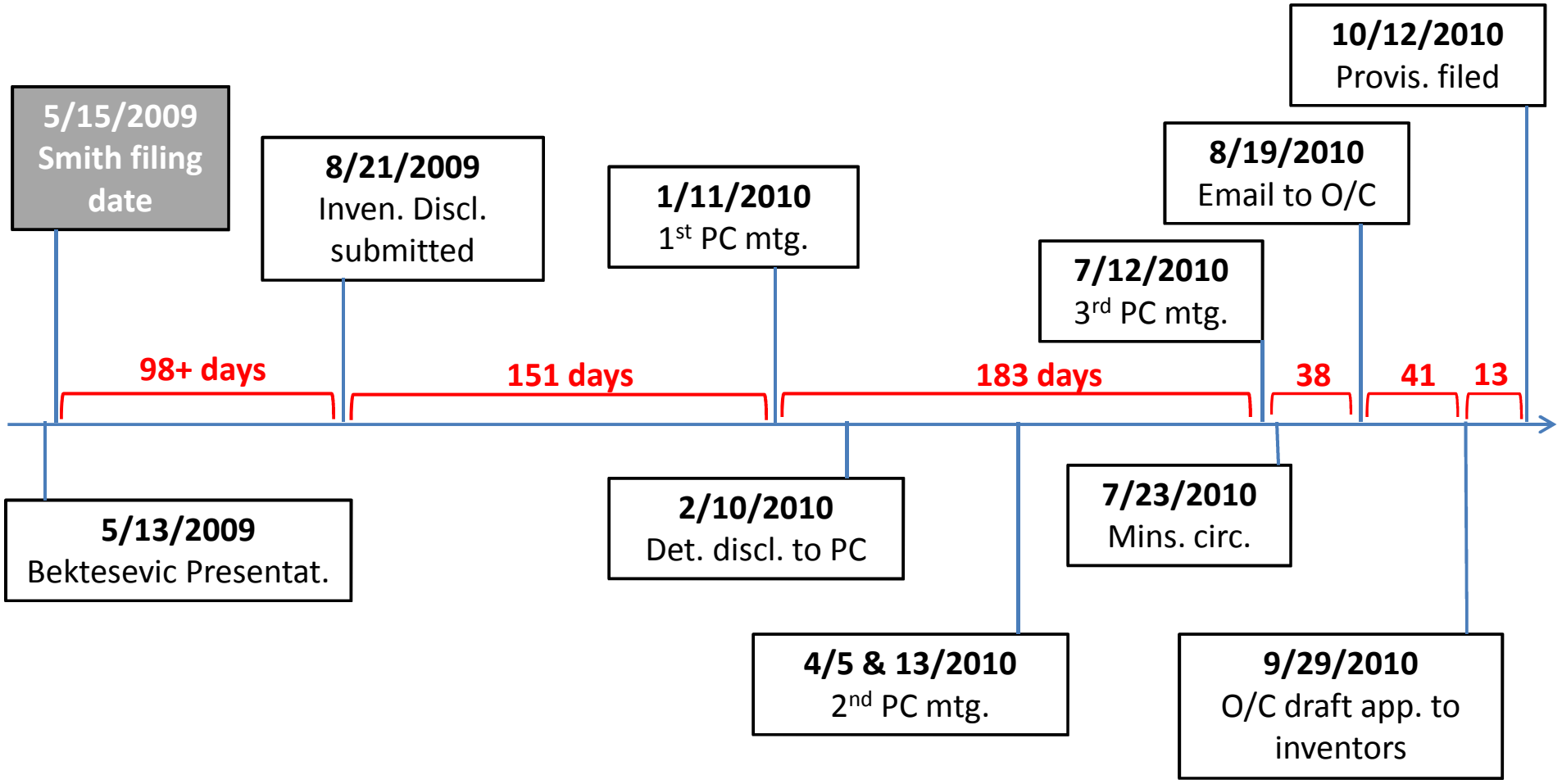
-915 Reply at 16-25

Sedat Critical Period (3 mos.)



-915 Reply at 18

Smith Critical Period (17 mos.)



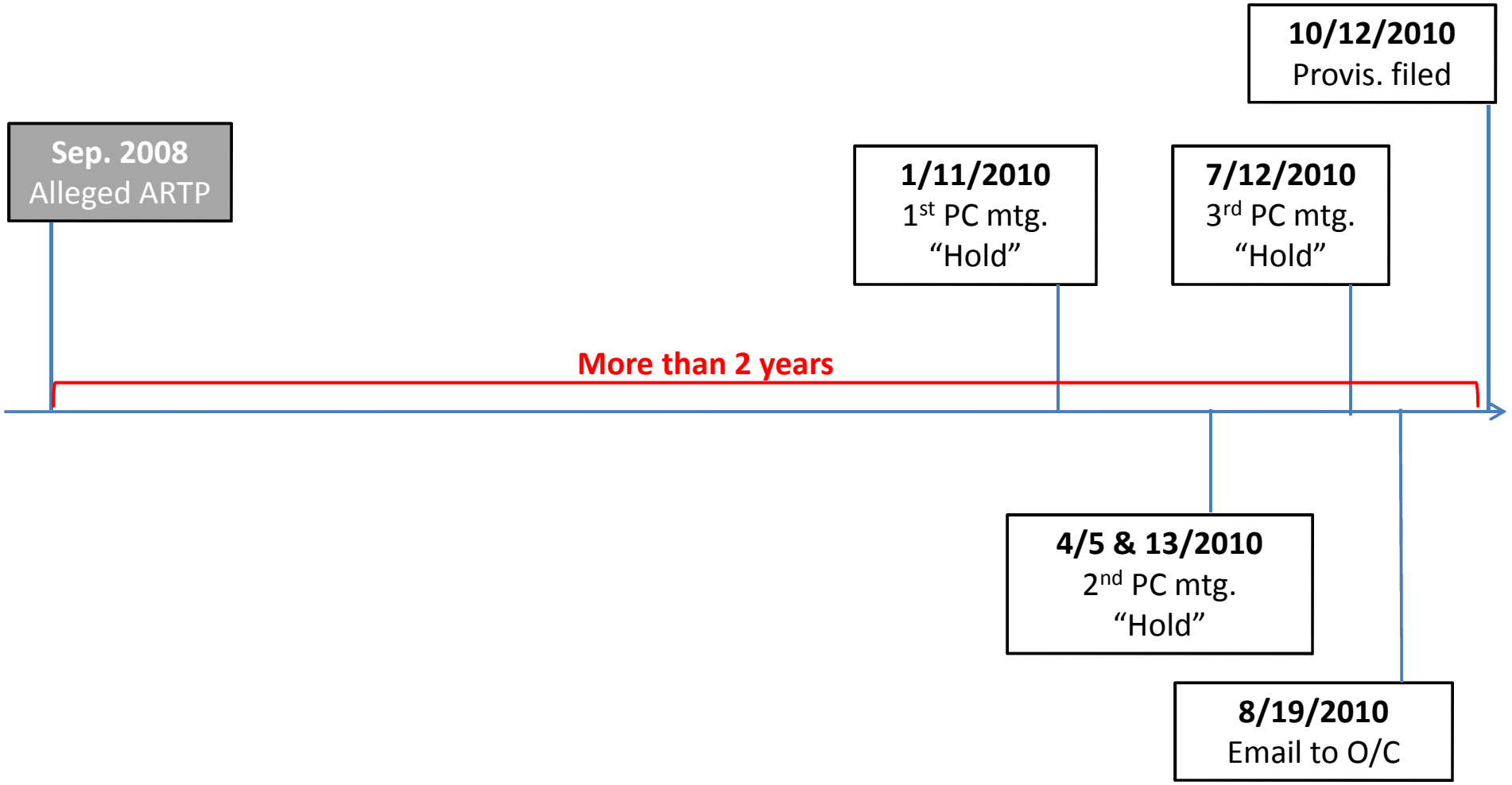
-915 Reply at 22

Morris Declaration Insufficient

- Lacks specificity required under *Olympus Am. Inc. v. Perfect Surgical Techniques, Inc.*, IPR2014-00233, Paper 56 (PTAB June 8, 2015).
  - Covers April 2009 thru 4Q 2011 in less than 2 pages
  - Does not specify dates of work
- Not related to practicing the process claimed in the '282 patent. *See Mycogen Plant Sci., Inc. v. Monsanto Co., 252 F.3d 1306 (Fed. Cir. 2001).*
  - Does not state that development efforts were related to the process claimed in the '282 patent
  - PO's counsel confirmed that Morris testimony was only intended to show general ongoing efforts to produce 1234yf, NOT to show development of the process of the '282 patent to produce 1234yf. *Ex. 1021 (4/12/2016 Call Transcript) at 13:9-13.*

-915 Reply at 20-21.

PO Abandoned, Suppressed, or Concealed Invention



-915 Reply at 25-28

Invalidity

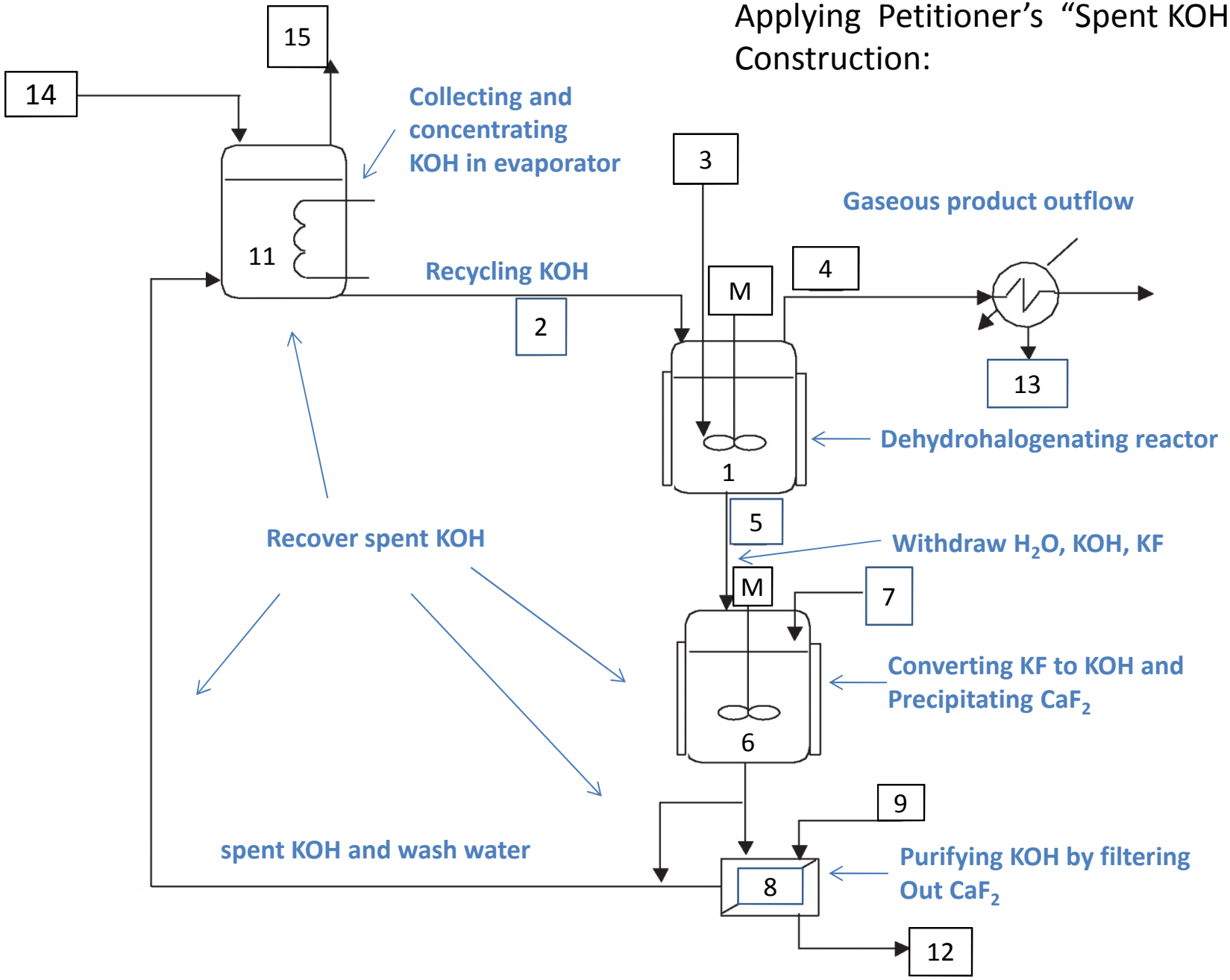
Grounds of Unpatentability

- Claims 21-27, 30-38, 41-46 are obvious over Sedat under 35 U.S.C. 103(a).
- Claims 1-20, 21, 28, 29, 36, 39, 40 are obvious over the combination of Smith and Sedat under 35 U.S.C. 103(a).
- Claims 1-46 are obvious over the combination of Smith, Masayuki, and Harrison under 35 U.S.C. 103(a).

Institution Decision – 915 at 18
Institution Decision – 916 at 17
Institution Decision – 917 at 17

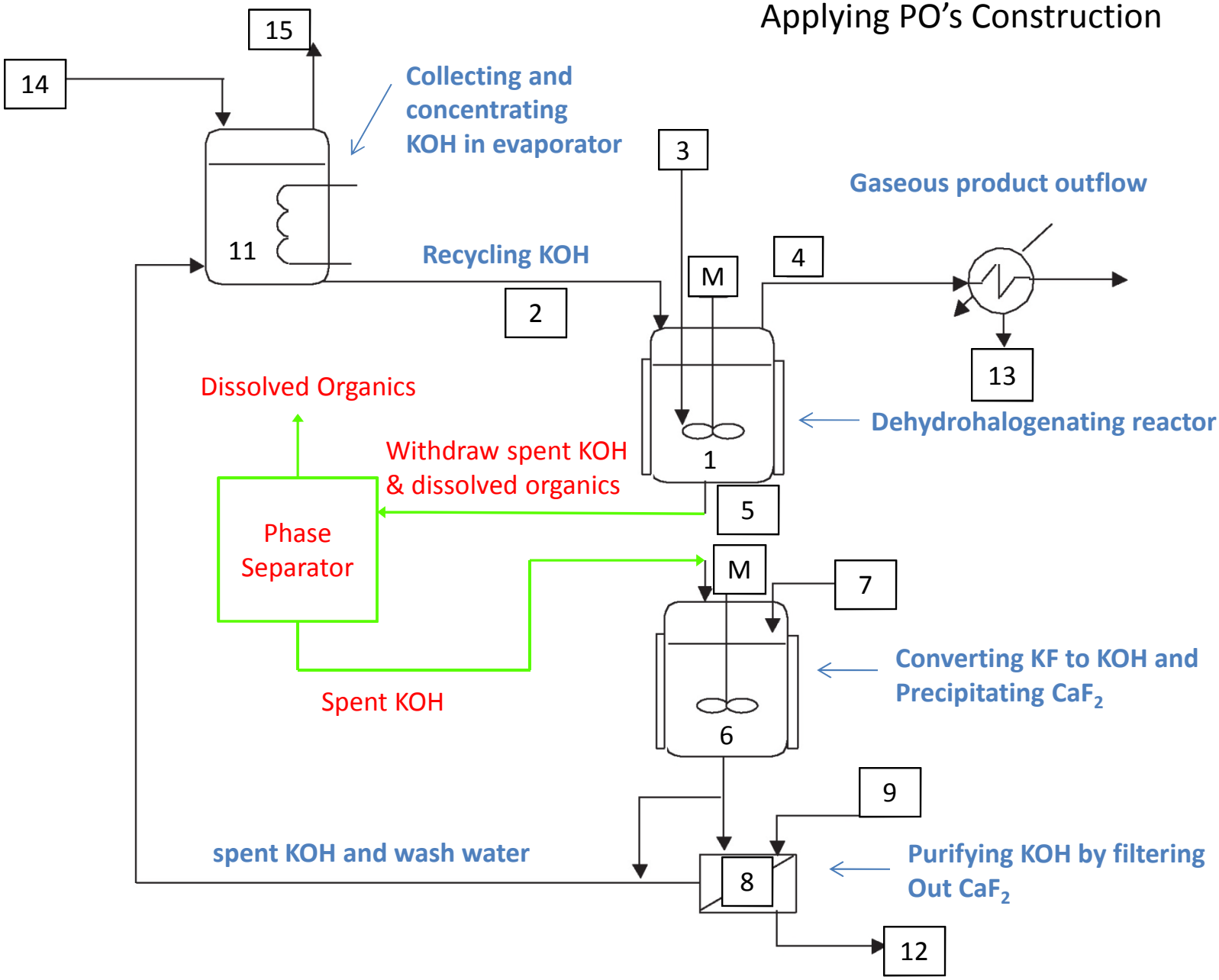
Claims 21-27, 30-38, 41-46 are obvious over Sedat under 35 U.S.C. 103(a)

Applying Petitioner's "Spent KOH" Construction:



Annotated Sedat Figure, -915 Petition at 19

Applying PO's Construction



Annotated Modified Sedat Figure, -915 Reply at 4

PO Expert Testimony concerning Dissolved Organics and Sedat

Q. So in your report you state that -- it's your opinion that there would be "***Organics entrained in the aqueous phrase [sic] reaction medium as a result of the shear mixing in Reactor 1***. In order to facilitate the reaction there would be no phase separation under these conditions.“

Would a person of ordinary skill in the art also recognize that reading Sedat?

A. I think so, yes.

-915 Ex. 1024, 110:10-18; -915 Reply at 2

PO Expert Testimony concerning Dissolved Organics and Sedat

- "Understanding that the term 'dissolved organics' is used in a dependent claim, ***I cannot understand a situation in which there would not be dissolved organics in a product or reaction stream***." (PO Expert discussing '282 patent)
- "It is my opinion that ***there would be organics entrained in the aqueous phase "reaction medium" as a result of the shear mixing in Reactor 1*** in order to facilitate the reaction and there would be no phase separation under these conditions." (PO Expert discussing Sedat)

-915 Ex. 2002, ¶¶ 96, 113; -915 Reply at 2

PO Expert Testimony concerning Dissolved Organics

Q. Why would it be undesirable to have dissolved or entrained organics present in Reactor 6 [of Sedat]?

***

A. -- with entrained organics, once you -- once you -- well, when you're in Reactor 6, it is not -- it's not doing anything. ***So why would you want to have your reagents go through Reactor 6 and not do anything when their next step is to go to 8 where you could potentially have them escape with your calcium fluoride.***

The other big issue there is most environmental permitting agents would have a big issue with having your organic in that system, because now you have -- you have -- you're handling a solid, and you have -- you have a path to escape out of a closed system. ***There could be a very big issue with -- with safety. Personnel could be exposed to this material, and just general escape into the environment. It's an environmental hazard.***

-915 Ex. 1024, 113:15-114:11; -915 Reply at 3.

PO Expert Testimony concerning dissolved organics and Sedat

Q: My question is just whether one of ordinary skill in the art would be able to remove dissolved organics by placing a typical decanter between Reactor 1 and Reactor 6 of Sedat?

THE WITNESS: They might substantially remove dissolved organics, but possibly not completely.

-915 Ex. 1024, 117:20-118:2 (objection omitted); -915 Reply at 5.

PO Expert Testimony concerning phase separation

Q. ... So in the work that you described, how did you know that you needed to decant in a continuous process?

A. How did -- how did -- that is common knowledge for lack of -- if you're -- ***if you're continuous*** and you need to -- well, ***you have to separate your phases***.

Q. And so that was common knowledge back in 2008?

A. Yes.

-915 Ex. 1025, 217:10-19; -915 Reply at 5.

PO Expert Testimony concerning phase separation

Q. What types of equipment would one typically use to achieve phase separation?
A. A decanter.

***

Q. What are known methods for separating organics like a phase-transfer catalyst?
A. A decanter --

-915 Ex. 1024, 36:2-4, 83:22-24; -915 Reply at 5; Ex. 1038 at 391.

Sedat Is Enabled

- PO Expert Testimony:
  - "shear mixing [is used] in Reactor 1 in order to facilitate the reaction" (Ex2002 (Lousenberg declaration), ¶113.)
  - 236ea *would* react with KOH in reactor 1 of Sedat to form 1225ye. (Ex1024 (Lousenberg deposition day 1), 154:17-20)
- U.S. Patent No. 9,018,429, which claims priority to Sedat and has the same reaction temperatures and pressures, issued and is presumed enabled.

-915 Reply at 6

Claims 1-20, 21, 28, 29, 36, 39, 40 are obvious over the combination of Smith and Sedat under 35 U.S.C. 103(a)

Motivation to Look Beyond Smith

- Appreciable amount of Unreacted KOH is withdrawn from DHF reactor
  - Steady state operation results in unreacted KOH being withdrawn from reactor
  - POSITA would use higher concentration of KOH in reactor to provide a higher reaction rate
  - Masayuki teaches recovery and recycle of spent DHA even when phase transfer catalyst is used
- Even small amount of unreacted KOH being withdrawn provides motivation to look beyond Smith
  - PO Expert admits at least small amount of unreacted KOH is withdrawn from Smith
  - Only 2 viable options for handling of aqueous stream comprising KOH and KF (sale of combined KOH/KF and conversion of KF)
  - PO Expert admits that responsible design chemist would investigate the 2 viable options. *See Bayer Schering Pharma AG v. Barr Labs., Inc.*, 575 F.3d 1341, 1350 (Fed. Cir. 2009).

-917 Reply at 1-5; -915 Ex. 1025 249:8-14, 242:22-25, 238:13-17, 246:5-247:5 (objections omitted)
-915 Ex. 1024 125:8-12, 135:24-136:6, 144:15-19 (objections omitted)

PO Expert Testimony Concerning KOH Concentration in a Continuous Reaction

Q. ... So the rate of reaction is based on the steady state concentration of KOH in the reactor; is that correct?

THE WITNESS: Yes.

***

Q. And the reaction at the interface [of the two phases] depends on the concentration of KOH in the aqueous [phase]; is that correct?

THE WITNESS: Yes.

Q. And if there's no KOH present, no reaction will occur, correct?

A. If there's no KOH present, no reaction will occur.

***

Q. Now, earlier you testified that you would want a high concentration of KOH in the reactor to make the reaction occur faster?

A. Right. High concentration in the aqueous phase.

-915 Ex. 1025, 249:8-14, 242:16-25, 238:13-17 (objections omitted); -915 Reply at 8.

PO Expert Testimony concerning Unreacted KOH being Withdrawn from Smith

Q. And when you withdraw that stream, that aqueous stream from the dehydrohalogenation reactor in Smith containing KOH and KF, won't KOH and KF both be present in that stream being withdrawn to make room for the fresh KOH?

A. …The concentration of KOH coming out of that -- in that reactor is very low…

Q. And what is very low in your opinion?

A. Probably -- if -- if we just look at the -- the ratio, mole ratio/weight ratio is probably very similar because they have similar molecular weights. ***About more than 90 percent would be KF.***

-915 Ex. 1025, 246:5-247:5; -915 Reply at 8.

Douglas "Conceptual Design of Chemical Processes" (1988)

"There is a rule of thumb in process design that it is desirable to recover more than 99% of all valuable materials. For initial design calculations we use the order of magnitude argument to say that *this rule of thumb is equivalent to requiring that we completely recover and then recycle all valuable reactants*."

-915 Ex. 1006 at 116-117; -915 Petition at 18-19

PO Expert Testimony concerning Options for Handling By-Product KF

Q: Is it correct that Smith teaches a by-product KF, and Sedat teaches how to convert KF back to KOH?

THE WITNESS: Yes.

***

Q. So of the three options, convert KF back to KOH, sell it, or dispose of it, disposing of it wouldn't make any sense, because it would cost more than selling it, correct?

A. Exactly. That's -- that's -- that's a negative dollar input to the process, whereas selling it is a positive dollar input to the process.

***

Q. So does that mean, as a responsible process design chemist, you wouldn't consider converting KF to KOH if you only have two options?

THE WITNESS: I would consider it.

-915 Ex. 1024, 125:8-12, 135:24-136:6, 144:15-19 (objections omitted); -915 Reply at 11.

Claims 1-46 are obvious over the combination of Smith, Masayuki, and Harrison under 35 U.S.C. 103(a)

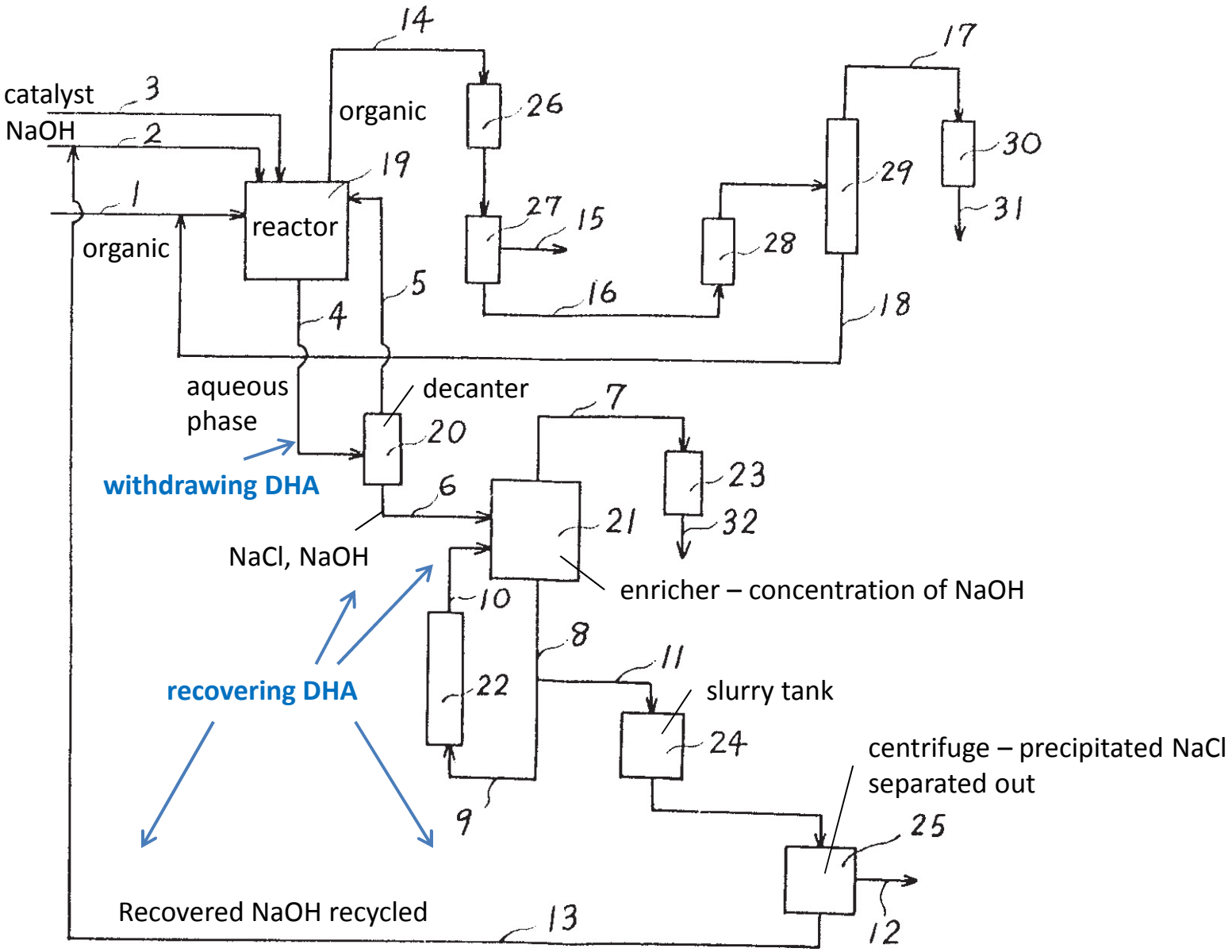
Motivation to Combine Smith, Masayuki, and Harrison

- POSITA would look for viable processing options for aqueous stream remaining after DHF reaction in Smith (PO Expert testimony)
  - sell combined KF and KOH
  - convert KF back to KOH and recycle KOH
- Masayuki teaches recycling dehydrohalogenating agent to reactor for reuse
- Harrison teaches converting KF to KOH using $Ca(OH)_2$
  - POSITA would know that KF and KOH cannot be separated because of similar solubilities and would know that reaction of Harrison would enable removal of KF (PO Expert testimony)

-915 Ex. 1024 125:8-12, 135:24-136:6, 144:15-19 (objections omitted)
-916 Ex. 1025, 288:13-289:5;

Expectation of Success in Combining Smith, Masayuki, and Harrison

Petition – Masayuki Figure Annotated



-917 Petition at 20

PO Expert Testimony concerning Combination of Smith and Masayuki

Q. What would be coming out of the reactor via Conduit 4 in Masayuki with the process of Smith being conducted in the dehydrohalogenation reactor?

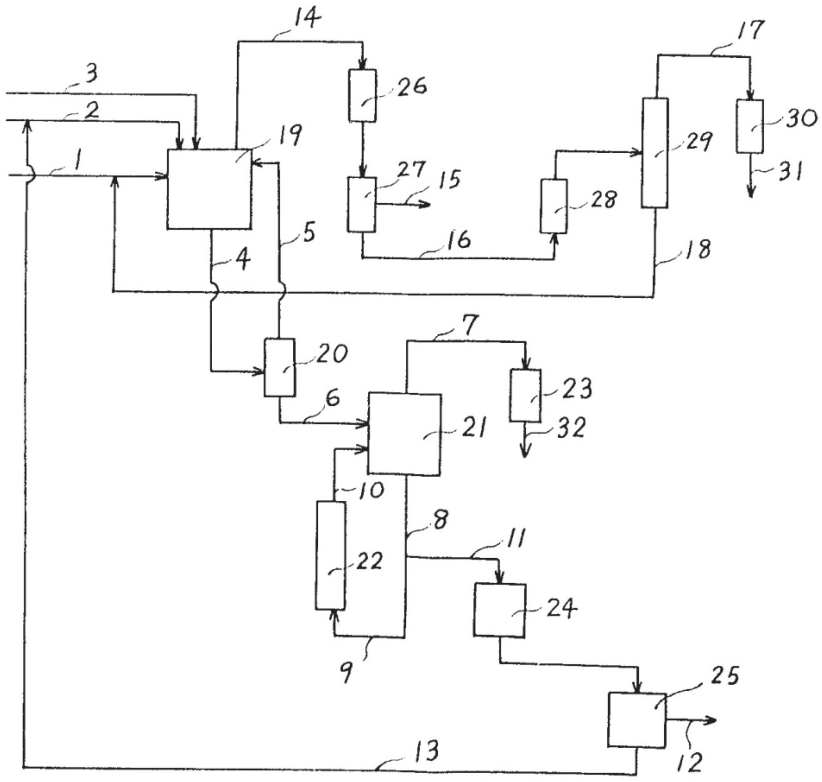
A. ***Aqueous KOH and the phase transfer catalyst and a very small amount of KOH***.

Q. Would there be any ***KF*** coming out of the reactor as well?

A. ***Yes***. That -- mostly what would be coming out of 4 would be aqueous KF.

Q. Would there be any ***dissolved organics*** coming out of Reactor 4?

A. ***Yes***.



-916 Ex 1025, 282:20-283:6; -916 Reply at 7.

PO Expert Testimony concerning Combination of Smith and Masayuki

Q. Would one of ordinary skill in the art understand that ***dissolved organics would be present in the stream, the aqueous stream coming out of Reactor 19*** if one were to conduct the dehydrohalogenation reaction of Smith in Reactor 19 of Masayuki?

THE WITNESS: ... Yes.

Q. ... Would one of ordinary skill in the art understand that ***it's desirable to remove dissolved organics present in the aqueous stream being removed from Reactor 19*** if the -- if the process of Smith were conducted in the flow diagram of Masayuki?

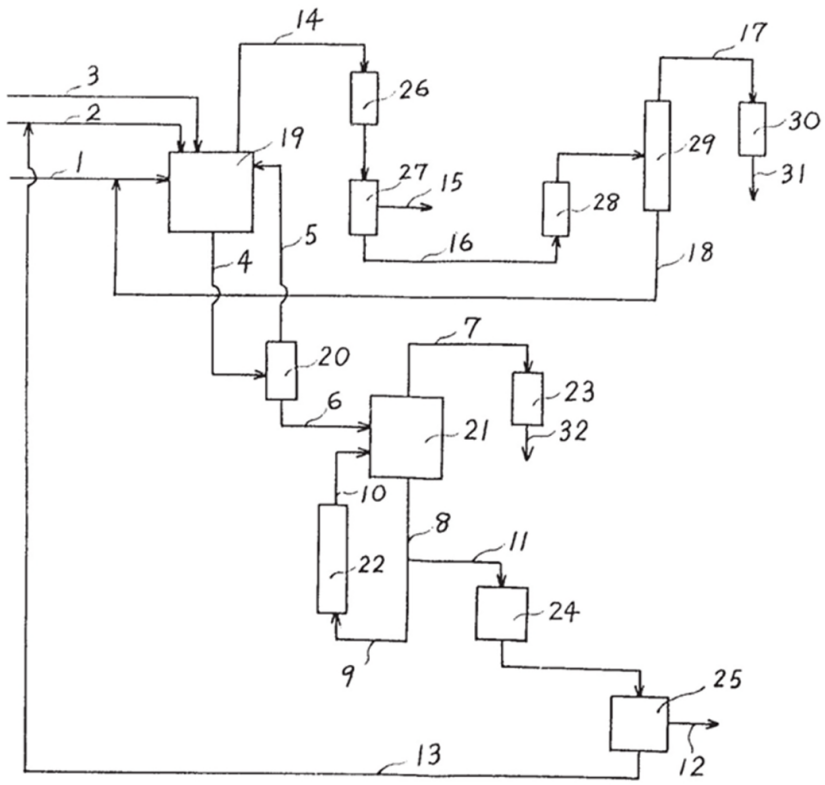
A. Yes.

-916 Ex. 1025, 292:9-293:5 (objections omitted); -916 Reply at 8-9

PO Expert Testimony concerning Combination of Smith and Masayuki

- Q. And what would happen in that decanter with the aqueous solution of KOH, KF and dissolved organics?

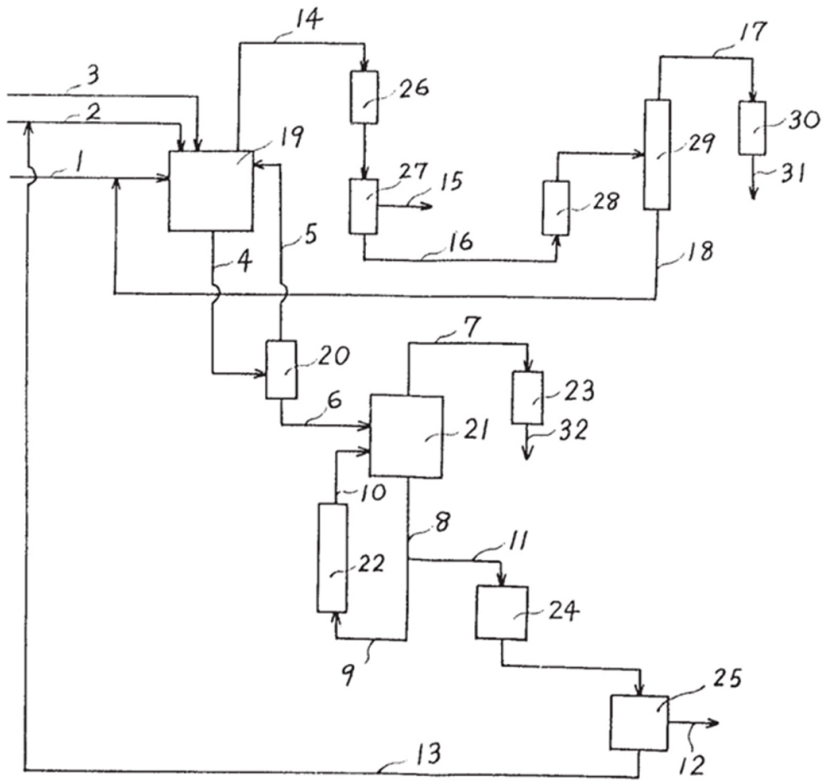
- THE WITNESS: The aqueous -- if it – in the -- in view of Masayuki, what would be happening there is ***the catalyst and the aqueous layer would be separating, and the catalyst would be returning to the reactor through Conduit 5***.



-916 Ex. 1025, 283:11-19 (objected omitted); -916 Reply at 7-8.

PO Expert Testimony concerning Combination of Smith and Masayuki

- Q. So the enricher would contain an aqueous solution of KF, KOH and dissolved organics?
- A. Yes.
  - ***
- Q. So if we were to conduct the reaction of Smith in the dehydrohalogenating reactor, deliver the aqueous phase from that reactor to the decanter through Conduit 4 and then deliver the aqueous phase from the decanter to the enricher and the enricher was operated at 100 degrees C, ***would you expect 236 and 245 to evaporate out of the enricher along with water***?
- A. ***Yes***, outside of Masayuki, ***that's what I would expect***. I don't know that it would happen, but that's what I would expect.



-916 Ex. 1025, 284:11-13, 285:13-23, -916 Reply at 8-9

PO Expert Testimony concerning Combination of Smith and Masayuki

Q. So for every mole of KF produced in the Formula 1 or the Formula 2 in column 12 of the '282 patent, you're going to produce 1 mole of water?

A. Correct.

***

Q. ... So you agree that ***the enricher would serve a purpose***?

A. ***Yes***. It -- it could be used to remove a small amount of water that was formed in the reaction....

-916 Ex. 1025, 181:3-6, 291:19-25, -916 Reply at 11.

PO Expert Testimony Concerning Combination of Smith, Masayuki, and Harrison

Q. Can you separate the KF and KOH in that aqueous solution that you've just described that would be present in the slurry tank?

A. Not efficiently.

Q. And why is that?

A. Because their solubilities are so similar.

Q. And is there a chemical reaction that one of ordinary skill in the art would be aware of that would convert KF to something else that would permit you to remove KF?

A. Sure. Reaction with calcium hydroxide.

Q. And that's a reaction that was known in 2008 or earlier; is that correct?

A. Yes, it is.

Q. And you've seen that reaction in a reference that I think you refer to as Harrison in your report; is that correct?

A. That's correct.

-916 Ex. 1025, 288:13-289:5; -916 Reply at 12-13.

Petitioner Expert Testimony Concerning Combination of Smith, Masayuki, and Harrison

Q. Did you consider any difficulties that might arise with an increasing concentration of KOH as higher and higher concentrations are circulated back to the reactor via conduits 13 and 2?

A. ***A POSITA would not have seen any difficulties that could not be overcome by further modeling or further evaluation of the components of the process***.

***

Q. And what do you base that opinion that a POSITA would not see any difficulties that could not be overcome?

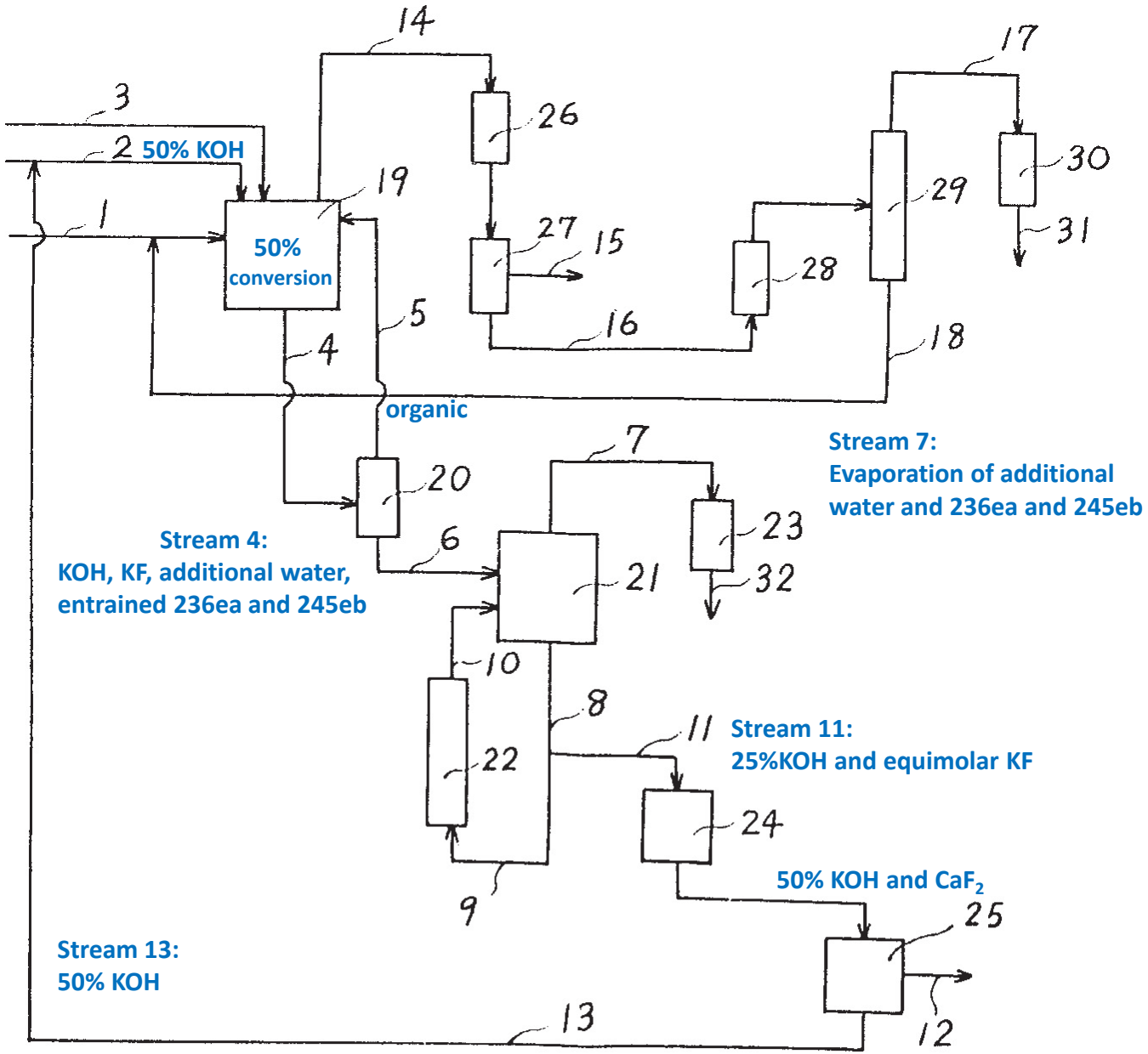
A. Well, a POSITA would look at that process of Masayuki and understand that ***from a variety of concentrations down to very low concentrations, the addition of lime would effectively precipitant calcium fluoride***.

Q. ... What I'm talking about is the increase of concentration of KOH by use of the enricher in combination with the conversion of KF into KOH in the slurry tank that would occur, and as the process repeats itself, would occur again and again and again?

A. Well, once again, I have not modeled it, but as I said previously, ***one could adjust the concentration in the enricher to maintain a desired level of KOH fed to the reactor***.

-916 Ex. 2005, 232:22-234:7 (objections omitted); -916 Reply at 10.

Reply - Masayuki Figure Annotated with PO Expert Example of 50% KOH and 50% Conversion



-916 Reply at 12

PO Expert Testimony concerning Combination of Smith, Masayuki, and Harrison

Q. ... Would an aqueous solution of 25 percent KF and 25 percent KOH in Slurry Tank 24 include any solid before lime is added?

A. ... What is the temperature of that slurry tank?

Q. Let's assume it's 100 degrees.

A. No, it would not precipitate.

Q. Would it precipitate at 50 degrees Celsius?

A. ... So a combined ***concentration of KOH and KF at 50 percent concentration at 50 degrees C would not precipitate***, but it's probably getting close to borderline.

-916 Ex. 1025, 294:7-295:1; -916 Reply at 13.