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**WO 2007/050745 A1**

(54) **Title:** INTERNAL OLEFINS PROCESS

(57) **Abstract:** This invention provides a process for making internal olefins which comprises isomerizing a feed comprising one or more internal olefin(s) in the presence of an isomerization catalyst to produce alpha olefins and reacting said alpha olefins in the presence of a dimerization catalyst to produce internal olefins.

**INTERNAL OLEFINS PROCESS**Field of the Invention

5           The present invention relates to a process for converting lower carbon number internal olefins into higher carbon number internal olefins.

Background of the Invention

10           Branched internal olefins have been made by structural or skeletal isomerization of linear olefins to their corresponding methyl branched isoolefins. U.S. Patent 5,510,306 describes one such process. Internal olefins have been made by dimerization of linear alpha olefins with a variety of dimerization catalysts.

15           In many commercial operations, lower carbon number internal olefins are produced. It would be advantageous to have a process which would convert these lower carbon number internal olefins, which are of low value, into higher carbon number internal olefins, preferably with some branching,  
20           which have a higher value and may be converted into the type of alcohols which may be used to make detergent products. The present invention provides such a process.

          U.S. Patent 6,291,733 describes a process for dimerizing alpha olefins to produce mostly linear internal olefins .  
25           This reaction is said to be highly selective. Internal olefins do not react by this dimerization process.

Summary of the Invention

          This invention provides a process for making internal olefins which comprises isomerizing a feed comprising one or  
30           more internal olefin (s) in the presence of an isomerization catalyst to produce alpha olefin (s), and reacting said alpha olefins in the presence of a dimerization catalyst to produce internal olefin (s) which have a higher carbon number than the feed internal olefin(s).

Detailed Description of the Invention

The product internal olefins may have a higher carbon number than the feed internal olefins and may be  $C_{6-40}$ ,  $C_{S-20r}$  or  $C_{12-18}$  linear and/or alkyl-branched internal olefins. The feed internal olefin (s) may have a lower carbon number than the product internal olefins and may be  $C_{4-24}$ ,  $C_{4-20f}$ ,  $C_{4-14r}$ ,  $C_{4-12r}$ ,  $C_{4-10}$ , or  $C_{4-8}$  internal olefins. The feed internal olefin stream may optionally contain one or more alpha olefin(s).

The isomerization in this process may be carried out in a different manner than isomerization is usually carried out. It is well understood that internal olefins may be reacted with an isomerization catalyst under isomerization conditions to produce alpha olefins (double bond isomerization).

It is also well understood that it is difficult to make alpha olefins in high conversion from internal olefins solely by an isomerization reaction. The reaction is an equilibrium reaction which favors the presence of internal olefins. In the present invention, the reaction produces alpha olefins from the starting feed of internal olefins. The alpha olefins are removed from the reaction mixture by dimerization to internal olefins and are replenished by the equilibrium of the isomerization reaction. The process of the invention may be carried out under conditions wherein the amount of alpha olefin (s) produced may be as high as possible, preferably the equilibrium amount of the alpha olefins in the isomerization reaction mixture or as close to the equilibrium amount as possible.

Contacting the alpha olefins with the dimerization catalyst allows the dimerization reaction of the alpha olefins to proceed to produce longer chain internal olefins (than the feed internal olefins) from the alpha olefins produced during the isomerization reaction. It is preferred that the dimerization and isomerization catalysts be

compatible with each other so as not to react such that the activity is reduced. Preferably, both catalysts should either be basic or acidic. For example, a homogeneous solution of a basic catalyst should not generally be mixed  
5 with a soluble acid catalyst. There are engineering solutions to enable the use of a solid acid and a solid base as long as they don't contact each other.

The isomerization conditions used herein may be chosen from a wide variety of catalysts and isomerization processes.  
10 Some of these processes include those described in U.S. patents 3,786,112, 4,749,819, 4,727,203, 5,107,047, 5,177,281, and 5,510,306, the disclosures of which are all herein incorporated by reference in their entirety. In instances that the isomerization reaction is separated from  
15 the reaction involving the dimerization catalyst, the conditions may include operating at a temperature of from 0 to 500°C, a pressure from 1 to 10,000 kPa, and, in a continuous process, a weight hourly space velocity of from 0.1 to 100. Generally, temperatures of 200°C or less may be  
20 sufficient and pressures of from atmospheric to 5000 kPa may be used. The thermodynamic equilibrium concentration of  $\alpha$ -olefins in an olefin mixture of the same carbon number increases as the temperature increases in the range of 0 to 500°C. The temperature may be as high as possible to  
25 maximize the amount of alpha olefins produced. However, the temperature should not be high enough to decompose the dimerization catalyst and/or the isomerization catalyst.

Almost any isomerization catalyst may be used but it is preferred that it be compatible with the dimerization  
30 catalyst chosen. Among the isomerization catalysts that may be used are the catalysts which are disclosed in U.S. Patents 3,786,112, 4,749,819, 4,727,203, 5,107,047 5,177,281, and 5,510,306, which are incorporated by reference.

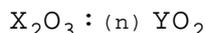
Suitable isomerization catalysts for use in this invention include catalysts comprising Group VIII noble metals, i.e., palladium, platinum, or ruthenium; niobium, or vanadium oxides; Group I, Group II, or Group III metal oxides including sodium oxide, potassium oxide, magnesium oxide, calcium oxide, zinc oxide, gamma-alumina, bauxite, eta-alumina, barium oxide, strontium oxide and mixtures thereof; and Group I metal carbonates on alumina.

Other isomerization catalysts which may be used include alumino silicate catalysts. A preferred alumino silicate catalyst is a ferrierite alumino silicate catalyst defined as having eight and ten member ring channels. Other preferred alumino silicates are ferrierite catalysts which are exemplified by the ZSM-35 alumino silicate described in U.S. Patent No. 4,016,245, the disclosure of which is incorporated herein by reference in its entirety, or by a piperidine derived ferrierite as described in U.S. Patent No. 4,251,499, the disclosure of which is herein incorporated by reference in its entirety. Other useful zeolites include Theta-1, ZSM-12, ZSM-22, ZSM-23, and ZSM-48. These alumino silicates may be associated with a catalytic metal, preferably selected from Group VIII or Group VIB of the periodic table. These metals may be exemplified by palladium, platinum, ruthenium, nickel, cobalt, molybdenum, osmium, and may be present in combination with one another. These catalytic metals may be present in quantities from 0.1 weight percent to 25 weight percent of the total catalyst composition.

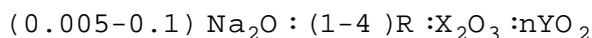
The ZSM-22 catalyst is more particularly described in U.S. Patent No. 4,556,477, the entire contents of which are herein incorporated by reference. The ZSM-23 catalyst is more particularly described in U.S. Patent No. 4,076,842, the entire contents of which are herein incorporated by reference .

The MCM-22 catalyst described in U.S. Patent 5,107,047 may also be used as the isomerization catalyst in the present invention. Zeolite MCM-22 may have a composition involving the molar relationship:

5



wherein X is a trivalent element, such as aluminum, boron, iron and/or gallium, preferably aluminum, Y is a tetravalent  
10 element such as silicon and/or germanium, preferably silicon, and n is at least 10, usually from 10 to 150, more usually from 10 to 60, and even more usually from 20 to 40. In the as synthesized form, zeolite MCM-22 may have a formula, on an anhydrous basis and in terms of moles of  $X_2O_3$  oxides per n  
15 moles of  $YO_2$  oxides, as follows:



wherein R is an organic component. The  $Na_2O$  and R components  
20 are associated with the zeolite as a result of their presence during crystallization, and are easily removed by post-crystallization methods. This zeolite, especially in its metal, hydrogen, and ammonium forms, can be beneficially converted to another form by thermal treatment.

25 In another embodiment, an alkali metal catalyst, preferably a sodium/potassium (NaK) catalyst, is used as discussed in U.S. Patent No. 4,749,819, which is herein incorporated by reference in its entirety. The preferred NaK catalyst is a eutectic mixture of sodium and potassium that  
30 is put on an alumina or silica support. A NaK catalyst may be made according to the teachings of U.S. Patent 3,405,196, which is herein incorporated by reference in its entirety, by

using a mixture of sodium and potassium as the alkali metal component .

As described above, the internal olefin feed may optionally contain some  $\alpha$ -olefins. In some embodiments of this invention, it may be preferred that  $\alpha$ -olefins be present in the feed. In one such embodiment, the  $\alpha$ -olefins may be ethylene, propylene, or a mixture thereof. The presence of these  $\alpha$ -olefins will allow the production of internal olefins having 6 or 7 carbon atoms .

In instances that the isomerization reaction is separated from the reaction involving the dimerization catalyst, the reaction involving the dimerization catalyst may be operated at temperatures up to 200°C, preferably from -10 to 100°C, and more preferably from 10 to 50°C. The pressure may range from 1 to 10,000 kPa, preferably from atmospheric pressure to 5000 kPa .

There are a variety of dimerization catalysts which may be used in the present invention. These catalysts include those described in U.S. Patents 4,252,987, 4,859,646, 6,222,077, 6,291,733, and 6,518,473, all of which are herein incorporated by reference. One such catalyst may comprise a dicyclopentadienyl halogenated titanium compound, an alkyl aluminum halide, and a nitrogen Lewis phase. Other such catalysts may include 1) a palladium compound, 2) a chelate ligand comprising a compound containing at least 2 nitrogen atoms which are connected through a chain comprising two or more carbon atoms, 3) a protonic acid, and 4) a salt of copper, iron, zinc, tin, manganese, vanadium, aluminum, or a group VIB metal. In another embodiment, the catalyst may be one wherein a metal, preferably nickel, is bound to at least one hydrocarbyl group or a catalyst which consists of complexes formed by admixing at least one nickel compound with at least one alkyl aluminum compound and optionally a

ligand. The catalyst may also be a catalyst comprising a combination of a nickel carboxylate or a nickel chelate with an alkyl aluminum halide or an alkyl aluminum alkoxide. Furthermore, catalysts for dimerization may be virtually any  
5 acidic material including zeolites, clays, resins,  $\text{BF}_3$  complexes,  $\text{HF}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{AlCl}_3$ , ionic liquids, super acids, etc.; and preferably a group VIII metal on an inorganic oxide support such as a zeolite support.

A preferred dimerization catalyst for use in the present  
10 invention is the transition metal catalyst/activating cocatalyst described in U.S. Patent 6,291,733, which is herein incorporated by reference in its entirety. The process conditions described in this patent and the catalyst used are highly selective to the dimerization of alpha  
15 olefins to mostly linear internal olefin dimers. The patent states that any transition metal complex with a cocatalyst may be used as catalyst in the process. The preferred embodiment is described as utilizing an activating cocatalyst which is alumoxane or a combination of a Lewis acid and an  
20 alkylating agent. The preferred cocatalyst is modified methyl alumoxane (MMAO) used in molar excess. The preferred transition metal complexes are said to be tridentate bisimine ligands coordinated to an iron center or a combination of an iron center and aryl rings, either substituted or  
25 unsubstituted. The most preferred catalysts are catalysts 1-5 shown at column 3 of the patent.

The effective amount of the preferred catalyst of U.S. 6,291,733 is relatively low. With the catalyst and  
cocatalyst comprising less than one percent by mass of the  
30 total alpha olefin mixture, the dimerization reaction occurs in minutes. A preferred catalyst concentration is from 0.01 to 0.1 mg of catalyst per ml of alpha olefin monomer. A more preferred catalyst concentration is from 0.02 to 0.08 mg per

ml of alpha olefin monomer and an even more preferred catalyst concentration is from 0.05 to 0.06 mg per ml of alpha olefin monomer.

Another preferred dimerization catalyst for use herein is described in U.S. Patent No. 4,658,078, which is herein incorporated by reference in its entirety. The catalyst may comprise zirconium or a hafnium metallocene and an aluminoxane wherein the atom ratio of aluminum to the total of zirconium and/or hafnium in the catalyst ranges from 1 to 100. The metallocenes used may have the general formula (cyclopentadienyl)<sub>2</sub>MY<sub>2</sub> wherein M is zirconium or hafnium and each Y is individually selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>5</sub> alkyl, C<sub>6</sub>-C<sub>20</sub> aryl and halogen. Preferably, Y is hydrogen, methyl, or chlorine. It is understood that the Ys may be the same or different. Included within the definition of the above cyclopentadienyl moiety is the lower alkyl (C<sub>1</sub>-C<sub>5</sub>)-substituted, preferably the methyl-substituted, cyclopentadienyl moiety. Specific examples of the metallocenes are dicyclopentadienyl dimethyl zirconium and bis (cyclopentadienyl) zirconium hydrogen chloride.

The isomerization reaction and the reaction involving the dimerization catalyst may take place in a batch or continuous process. These reactions may be carried out in separate reaction vessels or in the same reaction vessel. If the reactions take place in the same reaction vessel, they may take place consecutively or simultaneously.

In one embodiment of the present invention, in a batch reaction with the isomerization reaction proceeding to produce alpha olefin, the simultaneous reaction to produce longer chain internal olefins (having a higher carbon number than the feed internal olefins) from the alpha olefin may continue for a long period of time. The reaction may slow down when all of the original feed internal olefins are used

up because the dimerization reaction will produce such a wide variety of dimers, including many which will not react further.

In the case where the isomerization reaction and the reaction involving the dimerization catalyst take place in the same reaction vessel, in the same reaction zone or in different reaction zones and either consecutively or simultaneously, the reaction conditions may be selected to achieve both the desired isomerization and also to achieve the desired reaction involving the dimerization catalyst. In such case, the temperature may range from 0 to 200°C, preferably from 10 to 150°C, more preferably from 50 to 120°C. The reaction pressure may range from 1 to 10,000 kPa, preferably from atmospheric pressure to 5000 kPa, most preferably 100 to 1000 kPa. Generally, these temperatures are obtained by starting the reaction at room temperature and allowing the reaction exotherm to heat the solution.

In a preferred embodiment of the present invention, the isomerization and dimerization reactions may take place in the same reaction vessel. The catalysts used may be incompatible but preferably are compatible because then the reactions may be carried out in the same zone of the reaction vessel without the necessity of keeping the catalysts separated from one another. Normally incompatible catalysts may be made compatible in the same reaction vessel by keeping them separated in different zones, for example, by way of a membrane which allows the olefin to migrate but does not allow the catalysts to contact each other. The single reaction vessel may be a fixed bed reaction vessel, an autoclave, a chemically stirred tank reactor or a catalytic distillation column reactor. More than one reactor may be used. A stacked bed reaction system is one possibility. In such a system, the top bed would have one catalyst and the

lower bed would have another catalyst. This reaction may also be carried out in a series of reactors.

Alcohols derived from long chain olefins have considerable commercial importance in a variety of applications, including detergents, soaps, surfactants, freeze point depressants and lubricating oils, emollients, agricultural chemicals, and pharmaceutical chemicals. These alcohols are produced by any one of a number of commercial processes including the Oxo process and the hydroformylation of long chain olefins.

The internal olefins of this process may be converted into alcohols by the process described in U.S. Patent 5,849,960, which is herein incorporated by reference in its entirety. Olefins are contacted with an isomerization catalyst to yield an isomerized olefin. This product is converted, preferably by hydroformylation, into an alcohol. In addition to the catalyst described in this patent, many other known hydroformylation catalysts may also be used to convert the internal olefins of the present invention into alcohols.

Alcohols made from the product internal olefins made by the process of this invention are suitable for the manufacture of anionic, nonionic, and cationic surfactants. The alcohols may be used as the precursor for the manufacture of anionic sulfates, including alcohol sulfates and oxyalkylated alcohol sulfates, and nonionic oxyalkylated alcohols.

These alcohols may be utilized to make detergent compositions. Detergent compositions made from linear alcohols have long been known to exhibit excellent biodegradability. In recent years, there exists a growing need to find alcohol intermediates which are both biodegradable and exhibit good detergency at cold wash

temperatures. Alcohols containing some branching have become important. Such alcohols may be made from branched olefins, especially the branched internal olefins made according to the present invention.

5 Any technique for sulfating alcohols may be used herein. The alcohols may be directly sulfated or first oxyalkylated followed by sulfation. Sulfation and oxyalkylation processes are described in U.S. Patent no. 5,849,960, the entire text of which is herein incorporated by reference.

10 The sulfated alcohols may be used as surfactants in a wide variety of applications, including granular and liquid laundry detergents, dishwashing detergents, cleaning agents, liquid soaps, shampoos, and liquid scouring agents. They are generally comprised of a number of components besides the  
15 sulfated alcohols. These components may be other surfactants, builders, cobuilders, bleaching agents and their activators, foam controlling agents, enzymes, anti-greying agents, optical brighteners, and stabilizers. It is well known in the detergent and cleaning fields which of these  
20 components are preferred for use in any particular application.

The internal olefin products of the process of the present invention can be used in oil field drilling applications as the base oil in invert drilling fluids.

25 Internal olefin derivatives that can be made include alkyl benzene, alkyl xylene, detergent alcohols, plasticizer alcohols, alkenyl succinates, ether secondary alcohols, and diols and polyols produced by catalyzed dihydroxylation of internal olefins with the use of hydrogen peroxide.

30 The product internal olefins of this process may be converted into aldehydes by subjecting them to hydroformylating them with carbon monoxide and hydrogen in the presence of a hydroformylation catalyst, such as an Oxo

catalyst, to form an aldehyde. Alcohols can be made from the aldehydes by judicious selection of catalysts and operating conditions .

The dimerized internal olefins may also be used to  
5 alkylate aromatic hydrocarbons to produce alkyl aromatic hydrocarbons. This process involves contacting mono-olef ins with an aryl compound at alkylation conditions with an alkylation catalyst. For example, U.S. Patent 6,111,158, which is herein incorporated by reference in its entirety,  
10 describes such a process wherein the catalyst is a zeolite having an NES zeolite structure type.

#### EXAMPLES

##### Catalyst Preparation

The isomerization catalyst of Example 1 was made  
15 according to the procedure of Example I of U.S. Patent 3,405,196, which is herein incorporated by reference, with certain modifications as described below. One gram of 80 mesh (0.124 apertures per square millimeter) activated alumina was introduced into a flask from which water had been  
20 removed by placing the flask under vacuum overnight before use. The flask containing the alumina was heated to 50°C and then cooled to room temperature. All through this time it was kept under dry argon. One gram of a eutectic mixture of sodium and potassium (0.2g Na : 0.6g K by weight) was added  
25 to the flask. The mixture was heated to 80°C under argon for 15 minutes to melt the metal. The material in the flask changed color to a dark solid. Finally, it was cooled to room temperature.

The catalyst used in Example 2 contained sodium,  
30 potassium and silicon dioxide. It was obtained from SiGNa Chemistry, LLC, of Cherry Hill, New Jersey.

Reaction Feed

The internal olefin feed for both Examples 1 and 2 was a mixture of linear butenes, specifically cis-2-butene and trans-2-butene along with 15 percent by weight of 1-butene.

5 The feed contained 99.2% of butenes with the balance being primarily butanes.

Example 1

The internal olefin feed (10g) and the sodium/potassium/alumina isomerization catalyst were  
10 introduced into a stirred reaction vessel at room temperature and 101 kPa, substantially in the absence of air and water. This mixture was stirred and cooled to 0°C. After about 10 minutes, the butenes were transferred into a stirred stainless steel autoclave which contained the dimerization  
15 catalyst described in Illustrative Embodiment VIII of U.S. Patent 4,658,078, bis (cyclopentadienyl) zirconium hydrogen chloride (1.0g) . This mixture was allowed to react at 25°C and atmospheric to autogenic pressure kPa for about one hour. The resulting reaction mixture contained a 1-butene depleted  
20 mixture (less than 1 wt%) of 2-butenes, octenes, and a small amount of heavier oligomers (less than 1 wt%) .

Next, the dimers and unreacted butenes were cycled back to the stirred reaction vessel. The isomerization reaction in the stirred reaction vessel was allowed to continue at  
25 70°C and autogenic pressure kPa for about one hour at which time the reaction mixture was transferred to autoclave where further reaction with the dimerization catalyst took place at the same conditions for about one hour. After six cycles, the reaction was stopped and the reaction mixture was  
30 analyzed. The reaction mixture was cooled to 0°C and was filtered to remove solids from the liquid product. Upon analysis, 90 percent of the feed was converted to C<sub>8</sub> dimers,

trimers, etc. from which pure  $c_8$  dimer was distilled at atmospheric pressure.

Example 2

In this example, only one reaction container was  
5 utilized. The sodium/potassium/silica isomerization catalyst  
and the feed were introduced into the reaction container. 1  
gram of the dimerization catalyst, which in this case was  
dicyclopentadienyl dimethyl zirconium, was added to the  
reaction container at 0°C. The reactions were carried out at  
10 70°C and kPa autogenic pressure for 4 hours. At the end of  
that time the reaction mixture was cooled to 0°C, filtered to  
remove the solids, and the liquid organic products were  
removed and analyzed. 87 percent had been converted to  $c_8$   
dimers, trimers, etc. from which pure  $c_8$  dimer was distilled.  
15 Increasing the reaction time at a fixed temperature increases  
the ratio of trimers and heavier oligomers produced relative  
to the dimers. Decreasing the reaction time at a fixed  
temperature gives a higher ratio of dimers relative to  
trimers and oligomers but slows down the  
20 dimerization/oligomerization rate.

C L A I M S

1. A process for making internal olefin (s) which comprises isomerizing a feed comprising one or more internal olefin (s) in the presence of an isomerization catalyst to produce alpha olefin (s) and reacting said alpha olefins in the presence of a dimerization catalyst to produce internal olefin (s) which have a higher carbon number than the feed internal olefin (s).
2. The process of claim 1 wherein the amount of alpha olefins produced from the isomerization reaction is as close to the equilibrium amount of alpha olefins in the isomerization reaction mixture as possible.
3. The process of claim 1 wherein the temperature is from 0 to 200°C and the pressure is from 1 to 10,000 kPa.
4. The process of claim 1 wherein the isomerization reaction and the reaction in the presence of the dimerization catalyst take place in the same reaction vessel.
5. The process of claim 3 wherein the temperature is from 10 to 150°C.
6. The process of claim 4 wherein the temperature is from 50 to 120°C.
7. The process of claim 6 wherein the amount of alpha olefins produced is the equilibrium amount or less of alpha olefins in the isomerization reaction mixture.
8. The process of claim 1 wherein the isomerization reaction and the reaction which takes place in the presence of the dimerization catalyst are carried out in different zones of the same reaction vessel.
9. The process of claim 1 wherein the isomerization reaction and the reaction which takes place in the presence of the dimerization catalyst are carried out in separate reaction vessels.

10. The process of claim 9 wherein the isomerization reaction takes place at a temperature of 0 to 500°C and a pressure of 1 to 10,000 kPa.

5 11. The process of claim 9 wherein the dimerization reaction takes place at a temperature of up to 200°C and a pressure from 1 to 10,000 kPa.

10 12. The process of claim 1 wherein the isomerization and dimerization reactors take place in separate zones within the same reaction container wherein the zones permit the isomerized alpha olefins to move into the dimerization zone but prevent contact between the isomerization catalyst and dimerization catalyst.

13. The process of claim 1 wherein alpha olefins are present along with the feed internal olefins .

15 14. The process of claim 13 wherein the alpha olefins are selected from the group consisting of ethylene and propylene.

15. The process of claim 14 wherein the dimerized internal olefins produced have 6 or 7 carbon atoms .

20 16. The process of claim 1 wherein the feed internal olefins have from 4 to 24 carbon atoms and the dimerized internal olefins have from 6 to 40 carbon atoms.

17. The process of claim 16 wherein the feed internal olefins have from 4 to 20 carbon atoms and the dimerized internal olefins have from 8 to 20 carbon atoms.

25 18. The process of claim 17 wherein the feed internal olefins have from 4 to 14 carbon atoms and the dimerized internal olefins have from 12 to 18 carbon atoms.

30 19. The process of claim 1 wherein the dimerization catalyst is comprised of methyl alumoxane, tridentate bisimine ligands coordinated to an iron center or a combination of an iron center and aryl rings, either substituted or unsubstituted, and an alkylating agent.

20. The process of claim 1 wherein the dimerization catalyst comprises a metallocene having the general formula (cyclopentadienyl)  $2MY_2$  wherein M is zirconium or hafnium and each Y is individually selected from the group consisting of hydrogen,  $C_1-C_5$  alkyl,  $C_6-C_{20}$  aryl and halogen and an alumoxane wherein the atom ratio of aluminum to M in the catalyst ranges from 1 to 100.

21. A process for the production of alcohols which comprises first making internal olefins by the process of claim 1, contacting the internal olefins with an isomerization catalyst to yield isomerized olefins, and hydroformylating the isomerized olefins to produce alcohols.

22. A process for the production of sulfated detergents which comprises first making internal olefins by the process of claim 1, contacting the internal olefins with an isomerization catalyst to yield isomerized olefins, hydroformylating the isomerized olefins to produce alcohols, optionally oxyalkylating the alcohols, sulfating the alcohols, and combining the sulfated product with other detergent components.

# INTERNATIONAL SEARCH REPORT

International Application No  
**PCT/US2006/041767**

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C07C5/23 C07C5/25 C07C2/04 C07C2/34 C07C11/02  
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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**

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
<b>X</b>	US 2005/137435 A1 (TIITTA MARJA [FI] ET AL) 23 June 2005 (2005-06-23) the whole document -----	1-22

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  <b>16 February 2007</b>	Date of mailing of the international search report  <b>27/02/2007</b>
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Name and mailing address of the ISA/ 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	Authorized officer  <b>Cooper, Simon</b>
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2006/041767

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005137435 A1	23-06-2005	WO 2005061419 A1	07-07-2005