



- (51) **International Patent Classification:**
C07C 51/50 (2006.01) C07D 307/60 (2006.01)
- (21) **International Application Number:**
PCT/US2010/026203
- (22) **International Filing Date:**
4 March 2010 (04.03.2010)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
12/403,072 12 March 2009 (12.03.2009) US
- (71) **Applicant (for all designated States except US):** NALCO COMPANY [US/US]; 1601 W. Diehl Road, Naperville, Illinois 60563-1198 (US).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** SCHERTZER, Bryan, M. [US/US]; 2517 Prairie Court, Geneva, Illinois 60134 (US). MCGINNIS, Timothy, P. [US/US]; 1714 Childs Street, Wheaton, Illinois 60187 (US).
- (74) **Agents:** CARLSEN, Benjamin E. et al.; 1601 W. Diehl Road, Naperville, Illinois 60563-1198 (US).
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,

DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) **Title:** AN IMPROVED PROCESS FOR REACTING AN A, B-UNSATURATED DICARBOXYLIC ACID COMPOUND WITH AN ETHYLENICALLY UNSATURATED HYDROCARBON

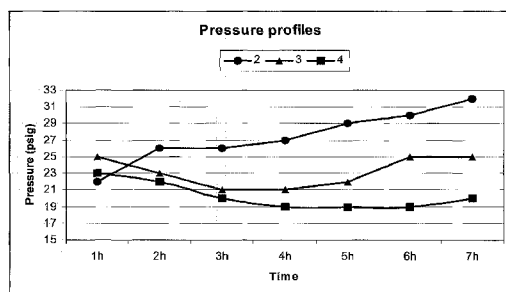


FIGURE 1

(57) **Abstract:** The invention provides an improved method of synthesizing chemicals according to the ene reaction. The method addresses two problems that previously could not be addressed simultaneously, preventing charring of the reaction, and preventing gaseous degradation of the reagents. The method involves adding a boron bearing compound and an aromatic/antioxidant compound to the ene reaction. Combining these two compounds together inhibits charring and also causes an effect that neither compound can accomplish alone. The addition of these two compounds together also more effectively prevents either of the reagents from degrading than when either reagent is added alone. As a result the method reduces costs by reducing the amount of reagents needed for a synthesis and further reduces costs by eliminating the need to filter out char from the end products of the ene reaction. The method is particularly useful in the ene reaction synthesis of ASA from olefins and maleic anhydride.

WO 2010/104738 A1

**AN IMPROVED PROCESS FOR REACTING AN α , β -UNSATURATED
DICARBOXYLIC ACID COMPOUND WITH AN ETHYLENICALLY UNSATURATED
HYDROCARBON**

Cross-Reference to Related Applications

None.

Statement Regarding Federally Sponsored Research or Development

Not Applicable.

Background of the Invention

This invention relates to compositions of matter and methods of using them to
10 reduce charring of reagents in the "ene" reaction. In the ene reaction a molecule is formed by the
reaction of an alkene reagent with an allylic hydrogen bearing reagent. The ene reaction is often
facilitated by the use of extreme reaction conditions such as high temperatures and/or strong
acids. One example of an ene reaction is the thermal reaction of reagents such as maleic
anhydride and an olefin to form alkenyl succinic anhydride product. Details of how to perform
an ene reaction are provided in US Patent Numbers 3,819,660, 3,219,666, 3,172,892, and
3,272,746.

Because of the extreme reaction conditions, ene reactions are often accompanied
by an unwanted "charring". Charring is the degradation of some of the reagents into an
insoluble, black, polymeric, solid, which resembles tar or charred material and is referred to as
20 "char". This degradation is sometimes accompanied by the evolution of gaseous byproducts.
The formation of char is problematic because it reduces the useful yield of the ene reaction, it
causes discoloration of the products, and it requires the addition of a filtration step after the ene
reaction to remove the char.

One previous attempt to prevent charring described in US Patent Numbers
4,736,044 and 4,086,251 involved adding boron or chlorine to the ene reaction. Another attempt
described in US Patent Number 3,412,111 involved the addition of phenols to the ene reaction.

A third attempt described in US Patent Number 3,476,774 involved the addition of anilines to the ene reaction. A fourth attempt described in US Patent Number 4,235,786 involved adding acid to the ene reaction. A fifth attempt described in European Patent EP 0 319 809 A2 involved adding a combination of butylated hydroxytoluene and oxalic acid to the ene reaction. The performance of these attempts however was unsatisfying because the additives reduced product yield by failing to inhibit charring completely and by partially degrading some of the reagents into gasses, leaving less raw material to produce the desired products.

The art described in this section is not intended to constitute an admission that any patent, publication or other information referred to herein is "prior art" with respect to this invention, unless specifically designated as such. In addition, this section should not be construed to mean that a search has been made or that no other pertinent information as defined in 37 C.F.R. § 1.56(a) exists. All patents or patent applications mentioned anywhere in this application are hereby incorporated by reference in their entirety.

Brief Summary of the Invention

At least one embodiment of the invention is directed towards a method for the chemical synthesis of products. The inventive method comprises reacting at least two reagents according to an ene reaction and adding to at least one of the reagents two compounds, one being a first compound and one being a second compound. The first compound is a boron bearing compound. The second compound is an aromatic or antioxidant-type compound. The first and second compounds are added in an amount effective in reducing char formation. The first and second compounds are added in an amount effective in reducing the degradation of at least one of the reagents into at least one gas by at least one of the compounds.

At least one embodiment of the invention is directed towards a method in which one of the reagents is an unsaturated α , β -dicarboxylic acid compound, one of the reagents is an unsaturated hydrocarbon, the boron bearing compound is boric oxide, and/or the

aromatic/antioxidant compound is selected from the list consisting of: BHT, a hindered phenolic compound, and a hindered aniline compound. In addition, any one or combination of some, or all of these aromatic compounds can be added. The boron bearing compound can be added into the ene reaction at a level in excess of 50 ppm. An antioxidant can also be added to the ene reaction as can an acid.

At least one embodiment of the invention is directed towards a method in which the ratio of boron bearing compound to aromatic compound is within the range of 8:1 to 21:1, the boron bearing compound is added to a level of 100 ppm, and/or the aromatic compound is added to a level of 1800 ppm. In at least one embodiment of the invention the product of the chemical synthesis is ASA, one of the reagents is maleic acid, one of the reagents is an olefin, and/or one of the reagents is a 16-24 carbon olefin. The first and second compounds can be added in an amount effective in reducing the degradation of at least one of the reagents into at least one gas selected from the list consisting of: carbon dioxide, carbon monoxide, and ethyne.

Detailed Description of the Invention

For purposes of this application the definition of these terms is as follows:

“ASA” means alkenyl succinic anhydride.

“Antioxidant” means any agent, which slows or prevents oxidative damage or oxidation.

“Boron Bearing Compound” means a compound containing Boron.

“BHT” is butylated hydroxytoluene.

“Char” means the resultants of those ene reaction reagents that rather than forming the desired product have instead degraded into an insoluble, black, polymeric, solid byproduct, which resembles tar or charred material.

“Charring” means the production of char.

“Ene reaction” means the addition of an enophile to an alkene through an allylic transposition and which is also known as “the Alder-ene reaction” and “ene synthesis”.

“Oxygen-Boron Bearing Compound” means a compound containing an Oxygen atom which is both bonded to a Boron atom and is bonded to another atom including but not limited to boric acids, boric acid anhydrides, boric acid esters, and boron oxide salts.

In the event that the above definitions or a definition stated elsewhere in this application is inconsistent with a meaning (explicit or implicit) which is commonly used, in a dictionary, or stated in a source incorporated by reference into this application, the application and the claim terms in particular are understood to be construed according to the definition in this application, and not according to the common definition, dictionary definition, or the definition that was incorporated by reference.

In at least one embodiment an ene reaction is conducted in the presence of a boron bearing compound and also in the presence of an aromatic/antioxidant compound. The combination of these two agents in the ene reaction produces an unexpected synergistic effect especially at ratios other than 1:1. The combination of these two compounds completely inhibits the formation of char which has been shown to increase product yield. The product yield increases because each of the two compounds prevents the other reactants from performing a degrading side reaction that would otherwise reduce the amount of reagent available for conversion into product.

In at least one embodiment the ene reaction is between an unsaturated α, β -dicarboxylic acid compound and an unsaturated hydrocarbon. In at least one embodiment the boron bearing compound is an oxygen-boron bearing compound. In at least one embodiment the boron bearing compound is boric oxide. In at least one embodiment, the aromatic compound is BHT, a hindered phenolic compound, or a hindered aniline compound. In at least on embodiment BHT, a hindered phenolic compound, a hindered aniline compound, or any combination thereof, are added to the ene reaction. In at least one embodiment the boron bearing compound is added

into the ene reaction at a level in excess of 50 ppm. In at least one embodiment an antioxidant is also added to the ene reaction. In at least one embodiment an acid such as boric acid is also added to the ene reaction.

In at least one embodiment, the proportions of the boron bearing compound relative to the aromatic/ antioxidant compound are such that they completely inhibit char formation. This proportion also reduces gaseous degradation of at least one of the reagents by either the boron bearing compound or the aromatic compound. One prior art method of using BHT together with boric acid as a char inhibitor for an ene reaction is described in US Patent Number 5,939,562. This prior art method however only utilized a 1:1 ratio of BHT with boric acid. A 1:1 ratio of the two has not been shown to be effective in producing the gaseous degradation reducing effect and completely inhibiting char. In at least one embodiment the ratio of boron bearing compound to aromatic/antioxidant compound is from between 8:1 to 21:1 by weight. US Patent Number 4,736,044 describes the use of other acids in reducing char but does not disclose completely inhibiting char.

By avoiding the reagent degradation effect, the ene reaction can be performed under different conditions than are commercially viable utilizing prior art methods. Prior art attempts at inhibiting charring involve running the ene reaction only for short lengths of time. This prevents both of the unwanted side effects (1- char formation and 2- gaseous degradation of reagents) from becoming too pronounced. By utilizing the aromatic/antioxidant compound and boron bearing compound in a proportion that displays the synergistic effect, both unwanted side effects can be avoided and the ene reaction can economically run for longer periods of time. Longer reaction times are more economical because they produce higher product yields.

In at least one embodiment, the reaction time is as long as 7 hours with no char. In at least one embodiment, the reaction time is as long as 10 hours with no char. In addition, the prior art discusses using a large excess of olefin reagent in the ene reaction to increase conversion and prevent charring. Such large excesses can often be as much as 50% to 100% of the molar

amount of maleic anhydride in typical ene reactions. In at least one embodiment the reaction requires far less olefin, such as levels as low as 20%-5% of the molar amount of maleic anhydride to high conversion without the formation of char.

The following examples are presented to describe embodiments, utilities of the invention, and the unexpected synergistic effect. These examples are in no way meant to limit the invention unless otherwise stated in the claims.

Table 1

| Sample | O/M A | BHT | B ₂ O ₃ | Time (hours) | Temp C | MA | Olefin | Resulting Char ** |
|--------|----------|-------|-------------------------------|-----------------|--------|------|--------|----------------------|
| 1 | 1.2:1 | 0.00% | 0.000% | 7 | 225 | 0.0% | 0.0% | 4* |
| 2 | 1.2:1 | 0.18% | 0.000% | 7 | 225 | 1.4% | 23.0% | 2 |
| 3 | 1.2:1 | 0.00% | 0.100% | 7 | 225 | 1.4% | 24.4% | 1 |
| 4 | 1.2:1 | 0.18% | 0.006% | 7 | 225 | 0.7% | 20.7% | 0 |

* Presumed based on Prior Art literature

** Scale for resulting char is:

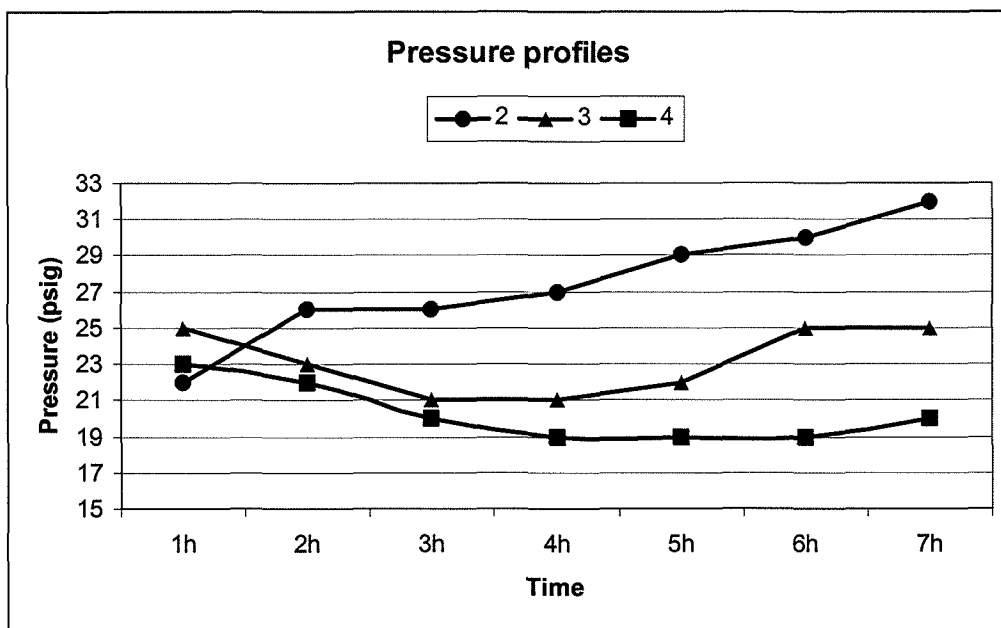
- 0 - Completely Inhibited, No char visible in product and when the ene product is run through a 100 μ m filter no char is deposited on the filter.
- 1 - Minimal Charring, No char visible in product, reactor is predominantly char free and when the ene product is run through a 100 μ m filter small amounts of char are deposited on the filter.
- 20 2 - Significant Charring, No char visible in product, reactor is coated with a thin layer of char and when the ene product is run through a 100 μ m filter the char clogs the filter.
- 3 - Much Charring, Some char is visible in product, reactor is coated with a thick layer of char and when the ene product is run through a 100 μ m filter the char clogs the filter.
- 4 - Excessive Charring, Large amount of char is visible in product, reactor is coated with a thick layer of char, multiple filtration steps are required before the ene product can be run through a 100 μ m filter.

30 Table 1 illustrates the results of four ASA producing thermal ene reactions involving reacting an 18 carbon olefin with maleic anhydride. A first control sample containing neither boric oxide nor BHT is presented based on the literature present in the Prior Art, which states that it would undergo excessive charring. In second sample BHT was added to the ene reaction at a level of 1800 ppm and significant charring was observed. In a third sample boric

oxide was added to the ene reaction at a level of 100 ppm and minimal charring was observed. However, in the second and third samples in which only boric oxide or only BHT were added, significant increases in the vapor pressure of the reactions occurred due to large amounts of carbon dioxide being evolved. The carbon dioxide evolution was a result of the respective decomposing of the reaction components. Some of the byproduct may also have evolved as carbon monoxide and ethyne. As a result, while boric oxide alone or BHT alone did reduce charring, they also reduced yield of ASA because each decomposed some component needed to produce ASA.

In the fourth sample the ene reaction was performed with 100 ppm boric oxide along with 1800 ppm BHT. In that reaction, vapor pressure declined until the reaction reached a high level of conversion. The reduction in pressure indicated that maleic anhydride was not being degraded into carbon dioxide or other gasses and instead was being consumed as it produced ASA. As a result, a greater yield of ASA was realized.

Graph 1



Graph 1 illustrates the pressure profiles of the samples presented in Table1. The graph shows that for the second and third prior art samples pressure rises more rapidly than in the fourth sample because they are undergoing decomposition into gasses. The fourth sample of the invention maintains low pressure up to the 7th hour indicating that product losing decomposition is not occurring.

While this invention may be embodied in many different forms, there are shown in the drawings and described in detail herein specific preferred embodiments of the invention. The present disclosure is an exemplification of the principles of the invention and is not intended to limit the invention to the particular embodiments illustrated. All patents and referenced
10 materials mentioned herein are incorporated by reference in their entirety. Furthermore, the invention encompasses any possible combination of some or all of the various embodiments described herein and incorporated herein.

The above disclosure is intended to be illustrative and not exhaustive. This description will suggest many variations and alternatives to one of ordinary skill in this art. All these alternatives and variations are intended to be included within the scope of the claims where the term "comprising" means "including, but not limited to". Those familiar with the art may recognize other equivalents to the specific embodiments described herein which equivalents are also intended to be encompassed by the claims.

This completes the description of the preferred and alternate embodiments of the
20 invention. Those skilled in the art may recognize other equivalents to the specific embodiment described herein which equivalents are intended to be encompassed by the claims attached hereto.

Claims

What is claimed is:

1. A method for the chemical synthesis of at least one product comprising:
reacting at least two reagents according to an ene reaction; and
adding two compounds to at least one of the reagents, one compound being a first
compound and one compound being a second compound; wherein:
the first compound is a boron bearing compound,
the second compound is an aromatic/antioxidant compound,
the first and second compounds are added in an amount effective in reducing char
10 formation, and
the first and second compounds are added in an amount effective in reducing the
degradation of at least one of the reagents into at least one gas by at least one of the compounds.
2. The method of claim 1 wherein one of the reagents is an unsaturated α, β -dicarboxylic
acid compound.
3. The method of claim 1 wherein one of the reagents is an unsaturated hydrocarbon.
4. The method of claim 1 wherein the boron bearing compound is boric oxide.
5. The method of claim 1 wherein the aromatic/antioxidant compound is selected from the
list consisting of: BHT, a hindered phenolic compound, and a hindered aniline compound.
6. The method of claim 1 wherein the boron bearing compound is added into the ene
20 reaction at a level in excess of 50 ppm.
7. The method of claim 1 wherein an antioxidant is also added to the ene reaction.
8. The method of claim 1 wherein an acid is also added to the ene reaction.
9. The method of claim 1 wherein the ratio of boron bearing compound to aromatic
compound is within the range of 8:1 to 21:1.
10. The method of claim 1 wherein the product of the chemical synthesis is ASA.
11. The method of claim 1 wherein one of the reagents is maleic anhydride.

12. The method of claim 1 wherein one of the reagents is an olefin.
13. The method of claim 5 further comprising adding one, some, or all of the other the aromatic/antioxidant compounds in the list.
14. The method of claim 1 in which the boron bearing compound is an oxygen-boron bearing compound.
15. The method of claim 1 in which the char formation is reduced to such an extent that when the product of the ene reaction is passed through a 100 μm filter, no char is deposited on the filter.

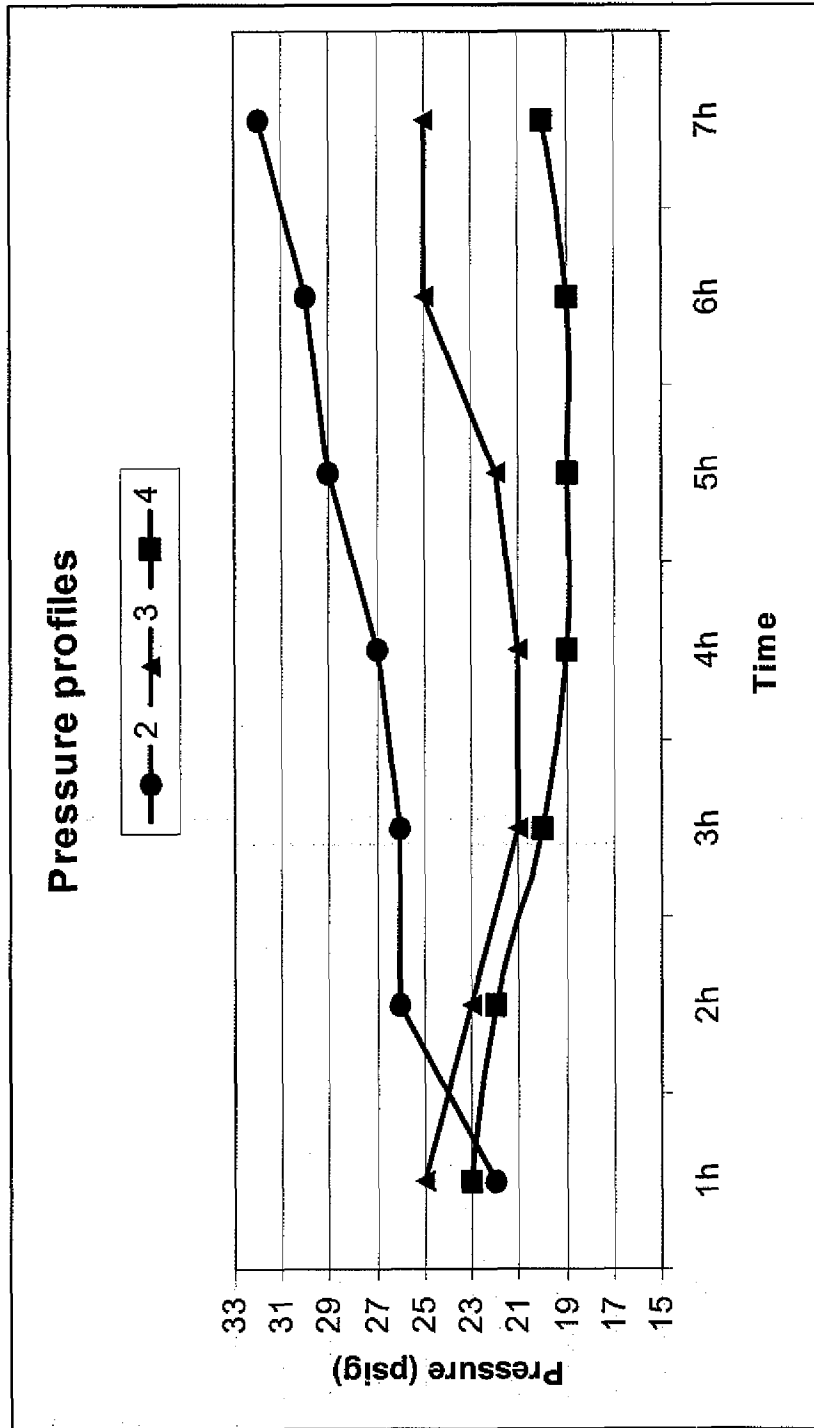


FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/026203

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C51/50 C07D307/60
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, BEILSTEIN Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| X | WO 96/11193 A1 (NESTE OY [FI]; KAPANEN MIKA [FI]; KOSKIMIES SALME [FI]; RANTANEN JAANA) 18 April 1996 (1996-04-18) Page 5, third paragraph; claim 16; examples 1,3-7; table 1 <p style="text-align: center;">-----</p> | 1-15 |

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

2 August 2010

Date of mailing of the international search report

09/08/2010

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentiaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Cooper, Simon

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/026203

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|--|------------------|-------------------------|---------------------------|
| WO 9611193 | A1 | 18-04-1996 | AT 261952 T 15-04-2004 |
| | | | AU 3653995 A 02-05-1996 |
| | | | CA 2201869 A1 18-04-1996 |
| | | | DE 69532721 D1 22-04-2004 |
| | | | DE 69532721 T2 13-01-2005 |
| | | | EP 0804429 A1 05-11-1997 |
| | | | FI 96418 B 15-03-1996 |
| | | | JP 10506909 T 07-07-1998 |
| | | | US 5939562 A 17-08-1999 |
| | | | |
