

Declarations under Rule 4.17:
— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(H))

Published:
— with international search report (Art. 21(3))

(54) Title: LUBRICATING COMPOSITION

(57) Abstract: The present invention provides a lubricating composition comprising: (i) a base oil; (ii) a non-silicone anti-foam agent; and (iii) one or more performance additives; wherein the composition has a kinematic viscosity at 100°C (according to ASTM D445) of 16.3 mmVs or less, a low temperature cranking viscosity of at most 6600cP at -30°C (ASTM D5293) and a NOACK volatility of at most 11% according to CEC-L-40-93.
LUBRICATING COMPOSITION

The present invention relates to a lubricating composition comprising a base oil and one or more performance additives for particular use in the crankcase of an internal combustion engine, in particular an internal combustion engine used in a passenger vehicle or light duty van.

In practice various lubricating compositions for crankcase engines are known. A disadvantage of known crankcase engine oils is that, especially when they are based on conventional mineral Group III base oils, they may have undesirable fuel economy oil performance values, it being problematic to blend to lower SAE J300 viscosity grades. A further problem of known crankcase engine oils is that they may have undesirable properties for one or more of wear performance and NOACK volatility, particularly when blending to lower SAE J300 viscosity grades.

Attempts have been made to overcome the above problems by formulating with non-mineral oil Group III base oils, such as Fischer-Tropsch derived base oils. WO2010020653 discloses the use of Fischer-Tropsch base oils in lubricating compositions. The composition of Example 1 of WO2010020653 shows a surprisingly low NOACK volatility when compared to the composition of Comparative Example 1 (using a Group III mineral base oil).

However, it has been found that in low viscosity formulations such as OW-30 and OW-40 engine oils, the use of Fischer-Tropsch base oils may not be enough on their own to provide the low NOACK volatility values desired for such formulations.
One way to further lower the NOACK volatility is to use a combination of polyalphaolefin base oils in addition to a Fischer-Tropsch derived base oil. However, polyalphaolefin base oils are relatively expensive and therefore it would be desirable to find an alternative way of lowering the NOACK volatility of OW-30 and OW-40 formulations, particularly those formulations comprising Fischer-Tropsch derived base oils.

It has surprisingly been found that by including a non-silicone anti-foam agent in the lubricating formulation the NOACK volatility can be lowered to desirable levels.

Hence according to the present invention there is provided a lubricating composition comprising:

(i) a base oil;
(ii) a non-silicone anti-foam agent; and
(iii) one or more performance additives;

wherein the lubricating composition has a kinematic viscosity at 100°C (according to ASTM D445) of 16.3 mm²/s or less, a low temperature cranking viscosity of at most 6600 cP at -30°C (ASTM D5293) and a NOACK volatility of at most 11% according to CEC-L-40-93.

According to another aspect of the present invention there is provided the use of a non-silicone anti-foam agent for reducing the NOACK volatility of a lubricating composition, in particular wherein the lubricating composition comprises a Fischer-Tropsch base oil.

Another important advantage of the present invention is that the lubricating composition has a desirably low cold-crank viscosity (i.e. dynamic viscosity according to ASTM D 5293), i.e. a cranking viscosity of at most 6600 cP at -30°C (ASTM D5293).

It is an advantage of the present invention that it
allows the formulation of alternative SAE J300 OW-30 and OW-40 crankcase engine oils.

There are no particular limitations regarding the base oil used in the lubricating composition according to the present invention, and various conventional mineral oils, synthetic oils as well as naturally derived esters such as vegetable oils may be conveniently used, provided that the requirements in respect of the lubricant composition according to the present invention are met.

The base oil used in the present invention may conveniently comprise mixtures of one or more mineral oils and/or one or more synthetic oils; thus, according to the present invention, the term "base oil" may refer to a mixture containing more than one base oil. Mineral oils include liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oil of the paraffinic, naphthenic, or mixed paraffinic/naphthenic type which may be further refined by hydrofinishing processes and/or dewaxing.

Suitable base oils for use in the lubricating oil composition of the present invention are Group III mineral base oils, Group IV poly-alpha olefins (PAOs), Group III Fischer-Tropsch derived base oils and mixtures thereof.

By "Group III" and "Group IV" base oils in the present invention are meant lubricating oil base oils according to the definitions of American Petroleum Institute (API) for category III and IV. These API categories are defined in API Publication 1509, 15th Edition, Appendix E, April 2002.

Fischer-Tropsch derived base oils are known in the art. By the term "Fischer-Tropsch derived" is meant that a base oil is, or is derived from, a synthesis product of a
Fischer-Tropsch process. A Fischer-Tropsch derived base oil may also be referred to as a GTL (Gas-To-Liquids) base oil. Suitable Fischer-Tropsch derived base oils that may be conveniently used as the base oil in the lubricating composition of the present invention are those as for example disclosed in EP 0 776 959, EP 0 668 342, WO 97/21788, WO 00/15736, WO 00/14188, WO 00/14187, WO 00/14183, WO 00/14179, WO 00/08115, WO 99/41332, EP 1 029 029, WO 01/18156 and WO 01/57166.

Synthetic oils include hydrocarbon oils such as olefin oligomers (including polyalphaolef in base oils; PAOs), dibasic acid esters, polyol esters, polyalkylene glycols (PAGs), alkyl naphthalenes and dewaxed waxy isomerates. Synthetic hydrocarbon base oils sold by the Shell Group under the designation "Shell XHVI" (trade mark) may be conveniently used.

Poly-alpha olefin base oils (PAOs) and their manufacture are well known in the art. Suitable poly-alpha olefin base oils that may be used in the lubricating compositions of the present invention may be derived from linear C₂ to C₃₂, preferably C₆ to C₁₆, alpha olefins. Particularly preferred feedstocks for said poly-alpha olefins are 1-octene, 1-decene, 1-dodecene and 1-tetradecene.

Preferably, the base oil as used in the lubricating composition according to the present invention comprises a Fischer-Tropsch derived base oil.

There is a strong preference for using a Fischer-Tropsch derived base oil over a PAO base oil, in view of the high cost of manufacture of the PAOs. Thus, preferably, the base oil contains more than 50 wt.%, preferably more than 60 wt.%, more preferably more than 70 wt.%, even more preferably more than 80 wt.%. most
preferably more than 90 wt.% Fischer-Tropsch derived base oil. In an especially preferred embodiment not more than 5 wt.%, preferably not more than 2 wt.%, of the base oil is not a Fischer-Tropsch derived base oil. In a preferred embodiment herein, the lubricating composition is essentially free of polyalphaolefin base oil, i.e. no more than 2 wt.% of the base oil is a polyalphaolefin base oil. In a particularly preferred embodiment herein, the lubricating composition is free of polyalphaolefin base oil. In another preferred embodiment herein 100 wt% of the base oil is based on one or more Fischer-Tropsch derived base oils.

The total amount of base oil incorporated in the lubricating composition of the present invention is preferably present in an amount in the range of from 60 to 99 wt.%, more preferably in an amount in the range of from 65 to 90 wt.% and most preferably in an amount in the range of from 70 to 85 wt.%, with respect to the total weight of the lubricating composition.

According to the present invention the base oil (or base oil blend) preferably has a kinematic viscosity at 100°C of at least 3.5 cSt (according to ASTM D445), preferably at least 3.8 cSt and most preferably at least 4.1 cSt.

The lubricating composition of the present invention further comprises a non-silicone anti-foam agent. As used herein the term "anti-foam agent" is a compound which is added into a lubricating composition at low levels (typically at a level of about 10ppm to about 500ppm) to help dissipate surface air bubbles.

Preferably, the non-silicone anti-foam agent is selected from acrylate, polyacrylate, and polymethacrylate (PMA) polymers. A preferred non-
silicone anti-foam agent for use herein is a polyacrylate anti-foam agent. As used herein the term polyacrylate anti-foam agent includes alkyl polyacrylate anti-foam agents and acrylic copolymers.

The non-silicone anti-foam agent is preferably present at a level of from 10ppm to 500ppm, preferably from 30ppm to 200ppm, more preferably from 100ppm to 200ppm, by weight of the lubricating composition.

An example of a suitable alkyl polyacrylate anti-foam agents is PC1644 commercially available from Cytec. PC1644 is an acrylic copolymer comprising ethylacrylate and 2-ethylhexylacrylate copolymer. Another commercially available alkyl polyacrylate anti-foam agent for use herein is PC2544 commercially available from Cytec. PC2544 is a modified acrylic copolymer.

As mentioned above, the lubricating composition according to the present invention meets certain specific requirements for the dynamic viscosity at -30°C, the kinematic viscosity at 100°C and the NOACK volatility.

Typically, the dynamic viscosity at -30°C (according to ASTM D 5293) of the composition is at most 6600 cP.

Typically, the dynamic viscosity at -35°C (according to ASTM D 5293) of the composition is at most 6200 cP.

Typically, the kinematic viscosity at 100°C (according to ASTM D 445) of the composition is at most 16.3 cSt, preferably from 9.3 to 16.3 cSt, more preferably from 9.3 and 12.5 cSt.

Typically, the high temperature, high shear viscosity ("HTHS"; according to ASTM D 4683) of the lubricating composition is in the range of from 2.9 to 3.7 mPa.s, preferably in the range of from 2.9 to 3.5 mPa.s.

Typically, the NOACK volatility (according to CEC-L-40-93) of the composition is 11 wt% or below, preferably
10.5 wt% or below, even more preferably 10.0 wt.% or below. Typically the NOACK volatility (according to CEC-L-40-93) is at least 8 wt.%.

The lubricating composition according to the present invention further comprises one or more additives such as anti-oxidants, anti-wear additives, dispersants, detergents, overbased detergents, extreme pressure additives, friction modifiers, viscosity index improvers, pour point depressants, metal passivators, corrosion inhibitors, demulsifiers, anti-foam agents, seal compatibility agents and additive diluent base oils, etc.

As the person skilled in the art is familiar with the above and other additives, these are not further discussed here in detail. Specific examples of such additives are described in for example Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pages 477-526.

A preferred additive is a silicone-based anti-foam agent which can be present on its own or as part of a performance additive package. The silicone-based anti-foam agent is preferably present at a level of from 20 to 200ppm, by weight of the lubricating composition.

A preferred silicone-based anti-foam agent is a polysiloxane. A silicone-based anti-foam agent is particularly useful herein in combination with a non-silicone anti-foam agent for providing a lubricating composition having reduced NOACK volatility.

Anti-oxidants that may be conveniently used include phenyl-naphthylamines (such as "IRGANOX L-06" available from Ciba Specialty Chemicals) and diphenylamines (such as "IRGANOX L-57" available from Ciba Specialty Chemicals) as e.g. disclosed in WO 2007/045629 and EP 1 058 720 B1, phenolic anti-oxidants, etc. The teaching of

Anti-wear additives that may be conveniently used include zinc-containing compounds such as zinc dithiophosphate compounds selected from zinc dialkyl-, diaryl- and/or alkylaryl- dithiophosphates, molybdenum-containing compounds, boron-containing compounds and ashless anti-wear additives such as substituted or unsubstituted thiophosphoric acids, and salts thereof.

Examples of such molybdenum-containing compounds may conveniently include molybdenum dithiocarbamates, trinuclear molybdenum compounds, for example as described in WO 98/26030, sulphides of molybdenum and molybdenum dithiophosphate.

Boron-containing compounds that may be conveniently used include borate esters, borated fatty amines, borated epoxides, alkali metal (or mixed alkali metal or alkaline earth metal) borates and borated overbased metal salts.

The dispersant used is preferably an ashless dispersant. Suitable examples of ashless dispersants are polybutylene succinimide polyamines and Mannich base type dispersants.

The detergent used is preferably an overbased detergent or detergent mixture containing e.g. salicylate, sulphonate and/or phenate-type detergents.

Examples of viscosity index improvers which may conveniently be used in the lubricating composition of the present invention include the styrene-butadiene stellite copolymers, styrene-isoprene stellite copolymers and the polymethacrylate copolymer and ethylene-propylene copolymers. Dispersant-viscosity index improvers may be used in the lubricating composition of the present invention.
Preferably, the composition contains at least 0.1 wt.% of a pour point depressant. As an example, alkylated naphthalene and phenolic polymers, polymethacrylates, maleate/fumarate copolymer esters may be conveniently used as effective pour point depressants. Preferably not more than 0.3 wt.% of the pour point depressant is used.

Furthermore, compounds such as alkenyl succinic acid or ester moieties thereof, benzotriazole-based compounds and thiodiazole-based compounds may be conveniently used in the lubricating composition of the present invention as corrosion inhibitors.

Compounds which may be conveniently used in the lubricating composition of the present invention as seal fix or seal compatibility agents include, for example, commercially available aromatic esters.

The lubricating compositions of the present invention may be conveniently prepared by admixing the one or more additives, including the non-silicone anti-foam agent, with the base oil(s).

The above-mentioned additives are typically present in an amount in the range of from 0.01 to 35.0 wt.%, based on the total weight of the lubricating composition, preferably in an amount in the range of from 0.05 to 25.0 wt.%, more preferably from 1.0 to 20.0 wt.%, based on the total weight of the lubricating composition.

Preferably, the composition contains from 10 wt.% to 15 wt.% of an additive package comprising a combination of additives including anti-oxidants, a zinc-based anti-wear additive, an ashless dispersant, an overbased detergent mixture, and a silicone-based anti-foaming agent.

According to an especially preferred embodiment of the present invention, the composition meets the requirements of an SAE J300 OW-30 or OW-40 formulation,
preferably those of a OW-30 formulation.

In another aspect, the present invention provides the use of a non-silicone anti-foam agent for reducing the NOACK volatility of lubricating composition, in particular wherein the lubricating composition comprises a Fischer-Tropsch derived base oil.

Also the present invention provides a method of improving NOACK volatility properties, which method comprises lubricating the crankcase of an engine, in particular a passenger car motor engine, with a lubricating composition according to the present invention.

The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

Examples

Lubricating Oil Compositions

Various engine oils for use in a crankcase engine were formulated.

Table 1 indicates the properties for the base oils used.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>Base oil 1 (GTL4)</th>
<th>Base oil 2 (GTL8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity at 100°C [cSt]</td>
<td>4.2</td>
<td>8.5</td>
</tr>
<tr>
<td>VI Index²</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>NOACK volatility³ [wt.%]</td>
<td>14</td>
<td>5</td>
</tr>
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</table>

¹According to ASTM D 445
²According to ASTM D 2270
³According to CEC L-40-A-93 / ASTM D 5800

Table 2 indicates the composition and properties of the fully formulated engine oil formulations that were
tested; the amounts of the components are given in wt.%, based on the total weight of the fully formulated formulations.

All tested engine oil formulations contained a combination of a base oil, an additive package (Additive Package 1), and a supplementary additive package (Additive Package 2), which additive packages were the same in all tested compositions.

Additive package 1 was Infineum P6660 commercially available from Infineum which contained a combination of additives including anti-oxidants, a zinc-based anti-wear additive, an ashless dispersant, an overbased detergent mixture, and a silicone-based anti-foaming agent.

Additive package 2 contained a combination of a dispersant, anti-oxidant and a friction modifier.

Examples 1 to 6 contained a non-silicone anti-foam agent. The non-silicone anti-foam agents were alkyl polyacrylate anti-foam agents with the tradenames PC1644 and PC2544 commercially available from Cytec.

Comparative Examples 2 to 4 contained a silicone-containing anti-foam agent (Synative AC AMH-2 commercially available from Cognis).

In all formulations, a conventional viscosity modifier concentrate was used to adjust the viscosity and a conventional pour point depressant was used to adjust the pour point.

"Base oil 1" was a Fischer-Tropsch derived base oil ("GTL 4") having a kinematic viscosity at 100°C (ASTM D445) of approx. 4 cSt (mm²s⁻¹).

"Base oil 2" was a Fischer-Tropsch derived base oil ("GTL 8") having a kinematic viscosity at 100°C (ASTM D445) of approx. 8 cSt (mm²s⁻¹).

These GTL 4 and GTL 8 base oils may be conveniently
manufactured by the process described in e.g. WO-A-02/070631, the teaching of which is hereby incorporated by reference.

The compositions of Examples 1 to 6 and Comparative Example 1 to 4 were obtained by mixing the base oils with the additive package and the anti-foam agent, where present, using conventional lubricant blending procedures.

The composition of Comparative Examples 1-4 and Examples 1-6 met the requirements of a OW-30 formulation, according to SAE J300.

The lubricating compositions of the Examples and Comparative Examples were subjected to various test methods as indicated in Table 2 in order to determine their NOACK volatility, their dynamic viscosity at -35°C and their kinematic viscosity at 100°C. The results are shown in Table 2.
<table>
<thead>
<tr>
<th>Component [wt. %]</th>
<th>Comp. Ex. 1</th>
<th>Comp. Ex. 2</th>
<th>Comp. Ex. 3</th>
<th>Comp. Ex. 4</th>
<th>Ex. 1</th>
<th>Ex. 2</th>
<th>Ex. 3</th>
<th>Ex. 4</th>
<th>Ex. 5</th>
<th>Ex. 6</th>
</tr>
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<tr>
<td>Additive Package 1</td>
<td>13.3</td>
<td>13.3</td>
<td>13.3</td>
<td>13.3</td>
<td>13.3</td>
<td>13.3</td>
<td>13.3</td>
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<tr>
<td>Additive Package 2</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
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<td>1.6</td>
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<td>Pour Point Depressant</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
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<td>Viscosity Modifier</td>
<td>7.8</td>
<td>7.8</td>
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<td>0.02</td>
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<td>-</td>
<td>-</td>
<td>0.003</td>
<td>0.01</td>
<td>0.02</td>
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<td>-</td>
</tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.003</td>
<td>0.01</td>
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<td>GTL 4</td>
<td>71</td>
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<tr>
<td>GTL 8</td>
<td>6</td>
<td>5.997</td>
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<tr>
<td>Vk100^1</td>
<td>12.06</td>
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<td>12.06</td>
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<td>Vd-35^2</td>
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<tr>
<td>NOACK^3, %/m</td>
<td>11.5</td>
<td>11.4</td>
<td>11.2</td>
<td>11.1</td>
<td>10.1</td>
<td>10.3</td>
<td>9.9</td>
<td>10.7</td>
<td>10.2</td>
<td>10.1</td>
</tr>
</tbody>
</table>

1. According to ASTM D445
2. According to ASTM D5293
3. According to CEC-L-40-93
Discussion

As can be learned from Table 2, Examples 1-6 containing a non-silicone anti-foam agent at 30ppm, 100ppm and 200ppm, have significantly lower NOACK volatility values than Comparative Examples 1-4 (not containing any non-silicone anti-foam agent).

An important advantage of the present invention is that OW-30 formulations meeting stringent NOACK volatility requirements (e.g. less than or equal to 10 wt.%) can be obtained without the need to use (relatively expensive) poly-alpha olefin (PAO) base oils.
1. A lubricating composition comprising:
   (i) a base oil;
   (ii) a non-silicone anti-foam agent; and
   (iii) one or more performance additives;
wherein the composition has a kinematic viscosity at
100°C (according to ASTM D445) of 16.3 mm²/s or less, a
low temperature cranking viscosity of at most 6600cP at
-30°C (ASTM D5293) and a NOACK volatility of at most 11%
according to CEC-L-40-93.

2. Lubricating composition according to claim 1,
wherein the composition has a NOACK volatility of at most
10.5% according to CEC-L-40-93.

3. Lubricating composition according to claim 1 or 2,
wherein the non-silicone anti-foam agent is selected from
acrylate, polyacrylate, and polymethacrylate (PMA)
polymers.

4. Lubricating composition according to any one of
claims 1 to 3, wherein the non-silicone anti-foam agent
is present at a level of from 10ppm to 500pm, by weight
of the composition.

5. Lubricating composition according to any one of
claims 1 to 4, wherein the base oil comprises one or more
Fischer-Tropsch derived base oils.

6. Lubricating composition according to Claim 5 wherein
the base oil comprises 80% or greater of one or more
Fischer-Tropsch derived base oils, by weight of the base
oil.
7. Lubricating composition according to any of Claims 1 to 6 wherein the composition is essentially free of polyalphaolefin base oil.

8. Lubricating composition according to any of Claims 1 to 7 wherein the one or more performance additives comprises a silicone-based anti-foam agent.

9. Use of a non-silicone anti-foam agent for reducing the NOACK volatility of a lubricating composition.

10. Use according to Claim 9 wherein the non-silicone anti-foam agent is an alkyl polyacrylate anti-foam agent.
### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>Y</td>
<td>wo 2010/020653 A2 (SHELL INT RESEARCH [NL]; COLBOURNE DAVID [GB]; WEDLOCK DAVID JOHN [GB]) 25 February 2010 (2010-02-25) cited in the application page 1, line 1 to page 2, line 13; page 4, line 25 to page 5, line 2; page 8, lines 23-26; page 10, lines 24, 25;; claims 1-3, 5, 7, 8, 10, 12</td>
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<td>Y</td>
<td>wo 2010/149706 Al (SHELL INT RESEARCH [NL]; DUNNING SIMON WILLIAM [GB]; WEDLOCK DAVID JOHN) 29 December 2010 (2010-12-29) page 1, lines 1-4; page 3, lines 12-18, 29-34; page 9, lines 27-30; page 12, line 26;</td>
<td>1-8</td>
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* Special categories of cited documents:

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**Date of the actual completion of the international search:** 13 June 2014

**Date of mailing of the international search report:** 24/06/2014

**Name and mailing address of the ISA:**
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Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

**Authorized officer:**
Renoth, Heinz
### DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>EP 2 457 985 Al (CHEVRON JAPAN LTD [JP]) 30 May 2012 (2012-05-30)</td>
<td>1-3,5-8</td>
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