

# PATENT SPECIFICATION

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## (54) BASE-OIL COMPOSITIONS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The invention is concerned with improving the daylight stability and/or oxidation stability of hydrocracked base oils.

It is known to prepare base oils, e.g. lubricating oils, transmission fluids or industrial oils, by subjecting various petroleum feedstocks, such as wax, vacuum distillates or residues or mixtures thereof, to one or more processing steps, in order to improve certain characteristics thereof.

One important processing step is that which increases the viscosity index (V.I.) of the feedstock.

For many years the V.I. of a feedstock has been increased by solvent extraction of the aromatic components thereof using solvents such as phenol, furfural or sulphur dioxide. The resultant base oil may be referred to as a solvent extracted based oil and usually has a V.I. in the medium (e.g. from 30 to 90) or high (e.g. from 90 to 120) V.I. range.

Recently, it has been proposed to increase the V.I. of a feedstock by the hydrocracking thereof. Generally, hydrocracking is an alternative process to solvent extraction. The base oils whose increase in V.I. have been obtained by the use of a hydrocracking step alone may be referred to as hydrocracked base oils and usually have V.I.'s in the high (e.g. 90 to 120), very high (e.g. 120 to 145) or extra-high (e.g. >145) range.

A problem of hydrocracked base oils, which is not encountered with solvent extracted base oils, is that they darken and/or form sludge when exposed to daylight i.e. to the short wave-length light characteristic of daylight. This phenomenon is usually described as daylight instability.

Various proposals have been made to improve the daylight stability of hydrocracked base oils, one of which is to add thereto various petroleum fractions such as a) conventional base oils, i.e. solvent-extracted feed stocks, which may have been subjected to a finishing treatment, such as a hydrofinishing treatment, b) vacuum distillates, c) deasphalted vacuum residues or d) aromatic extracts thereof, e.g. see U.K. Patent Specification 1,237,291. Whilst such fractions sometimes do improve the daylight stability to some extent it has surprisingly been found that the daylight stability can be improved still further.

Accordingly, the present invention is concerned with a base oil composition comprising

- (a) a hydrocracked base oil (as defined hereinafter), and  
(b) from 0.01 to 20 %w, based on weight of (a), of a hydrotreated extract of a vacuum distillate or of a deasphalted vacuum residue (all as defined hereinafter).

The term "hydrocracked base oil" as used herein means a base oil which has been hydrogenated under such conditions that the V.I. of the base oil increases by at least 1.5 for distillate base oils and by at least 10 for residual base oils as a result of the hydrogenation treatment. The term "hydrotreated extract of a vacuum distillate or of a deasphalted vacuum residue" means an extract of a vacuum distillate or of a deasphalted vacuum residue which has been hydrogenated under any conditions.

The hydrocracked base oils are obtained by treating the appropriate feedstock e.g. a vacuum distillate or a deasphalted residue of vacuum distillation, suitably derived from a

paraffinic crude oil, with hydrogen under conditions such that the V.I. of the feedstock, which is usually in the range of 30 to 80, is increased substantially. The V.I. usually increases by at least 20 units. This increase is accompanied by a structural alteration of the feedstock. As explained above the feedstock or the hydrocracked base oil is not subjected to a solvent-extracting step. The hydrocracking temperature is usually between 350°C and 500°C, the hydrocracking pressure is usually between 60 and 200 bars and the space velocity is usually between 0.1 to 2.0 kg feed per litre of catalyst per hour. The hydrocracking catalyst usually consists of one or more of the metals molybdenum, chromium, tungsten, vanadium, platinum, nickel, copper, iron and cobalt or their oxides and/or sulphides, either unsupported or supported on a suitable carrier, such as alumina or silica. Particularly advantageous catalysts are the iron transition metals (iron, cobalt and nickel) and the Group VIB metals (chromium, molybdenum and tungsten) especially combinations of metals from each of these groups, for instance cobalt and molybdenum, nickel and tungsten, and nickel and molybdenum supported on alumina. The catalyst may also contain promoters, such as compounds containing phosphorus, fluorine or boron.

The hydrotreated aromatic extract is obtained by the hydrogenation of the extracts of vacuum distillates or deasphalted vacuum residues, i.e. deasphalted residues of vacuum distillations, derived from crude oils in particular paraffinic crude oils. Suitable extracts are those obtained during the preparation of solvent extracted high V.I. base oils. Such extracts are suitably obtained by the solvent extraction, e.g. with phenol, furfural or sulphur dioxide, of feedstocks having an aromatic content in the range of from 30 to 60 %w. The extracts themselves, after removal of solvent, usually have aromatic contents of at least 90%w. Preferred extracts are those obtained by the solvent extraction of deasphalted vacuum residues i.e. bright stock extracts. The extracts may be hydrogenated under substantially the same conditions as described above for the production of hydrocracked base oils. Preferred hydrotreating temperatures are from 260 to 390°C and preferred hydrotreating pressures are from 80 to 170 bars. The space velocity may range from 0.1 to 2.0 kg feed per litre of catalyst per hour. The hydrotreated extracts may be subjected to a distillation step in order to remove the more volatile components therefrom. For example, the volatile material boiling between 200°C and 350°C may be removed before the hydrotreated extract is mixed with the hydrocracked base oil. The hydrotreated extracts may also be subjected to a dewaxing step. Mixtures of hydrotreated extracts of distillates and hydrotreated extracts of residues may be used as well.

The hydrocracked base oil from which the compositions of the invention are obtained may be, or may have been, subjected to one or more additional processing steps such as a finishing step and/or a distillation step and/or a dewaxing step. Dewaxing serves to decrease the pour-point of the feedstocks by removing wax therefrom and is usually carried out after the hydrocracking step. Finishing steps include clay and/or acid treatments and/or a hydrofinishing treatment. Preferred hydrocracked base oils for use in the present invention are those which have been hydrofinished. Usually such hydrocracked base oils are hydrofinished at temperatures between 200°C and 350°C and at pressures between 30 bars and 200 bars using catalysts of the same type as described above for the preparation of hydrocracked base oils.

The base oil compositions of the present invention may be prepared by any suitable method. One preferred method comprises mixing the hydrocracked base oil with the hydrotreated extract of a vacuum distillate or of a deasphalted vacuum residue. In this case the components of the mixture may be distilled and/or dewaxed before they are mixed or the mixture obtained may be distilled and/or dewaxed in the manner described above.

Another preferred method comprises mixing a hydrocracked base oil with an extract of a vacuum distillate or of a deasphalted vacuum residue and hydrogenating the mixture so as to hydrotreat simultaneously the hydrocracked base oil and the extract of the distillate or residue. The mixtures so obtained may be distilled and/or dewaxed in the manner described above.

As stated above the purpose of distilling the various hydrogenated materials is to remove therefrom the more volatile components.

Suitably the base oil compositions, which are suitably high viscosity index base oil compositions, comprise from 0.1 to 10 %w of the hydrotreated fraction, based on weight of the hydrocracked base oil.

The base oil compositions of the present invention are suitably used as lubricating oil compositions for internal combustion engines and in this respect may contain one or more of the conventional lubricating oil additives such as viscosity index improvers, anti-wear/extreme-pressure additives, detergents, anti-rust additives, anti-oxidants e.g. secondary amines, pour-point depressants and other daylight stabilizers such as quinones (e.g. tetrabutylidiphenquinone).

The invention will now be illustrated by reference to the following Examples.

In the Examples the hydrogenation catalyst used was a Ni/W alumina supported catalyst.

**EXAMPLES 1 to 9**

In these examples the components of the compositions were as follows.

Hydrocracked base oil A: Obtained by hydrocracking, hydrofinishing, distilling and dewaxing a vacuum distillate, having a V.I. of about 60, of a paraffinic crude oil. The hydrocracked and hydrofinished base oil had a V.I. of 98 and a viscosity of 7.29 centistokes at 210°F.

Hydrocracked base oil B: As for base oil A except that the distillate had a V.I. of about 48 and that the hydrocracked and hydrofinished base oil had a viscosity index of 99 and a viscosity of 5.17 centistokes at 210°F.

Aromatic extract (1): Derived by furfural extraction of a deasphalted vacuum residue, having an aromatic content of about 35 %w, derived from a paraffinic crude oil.

Hydrotreated aromatic extract A: Obtained by hydrotreating aromatic extract (1) at a temperature of 350°C, a pressure of 150 bars and a space velocity of 0.7 kg feed/litre catalyst/hour. The hydrotreated extract was distilled, to remove components having a boiling point of below about 250°C and was then dewaxed with a mixture (50/50) of MEK and toluene.

Hydrotreated aromatic extract B: As for hydrotreated aromatic extract A except that the hydrotreating temperature was 375°C.

Hydrotreated aromatic extract C: As for hydrotreated aromatic extract A except that the hydrotreating temperature was 385°C.

Aromatic extract (2): Derived by furfural extraction of a vacuum distillate (boiling point range 460 to 530°C), having an aromatic content of about 66 %w, derived from a paraffinic crude oil.

Hydrotreated aromatic extract D: Obtained by hydrotreating aromatic extract (2) at a temperature of 375°C, a pressure of 100 bars and a space velocity of 0.7 kg feed/litre catalyst/hour. The hydrotreated extract was distilled, to remove components having a boiling point of below 320°C and was then dewaxed with a mixture (50/50) of MEK and toluene.

High viscosity index base oil compositions according to the invention were obtained by mixing the hydrocracked base oils with the hydrotreated aromatic extracts in the amounts specified in Table I.

The base oil compositions were then subjected to an artificial daylight stability test which comprised irradiating by means of two 40 W fluorescent tubes, Pyrex ("Pyrex" is a Registered Trade Mark)/ASTM pour point test tubes containing 30 g of the base oil which were maintained at a temperature of  $35 \pm 0.5^\circ\text{C}$ . The time taken for haze or sludge formation to occur was noted. The results are given in Table I.

For comparison the results obtained using the hydrocracked base oils alone ((a) and (d)) and mixtures of the hydrocracked base oils and the unhydrotreated aromatic extracts ((b), (c), (e), (f) and (g)) are also given in Table I. (The percentages by weight are based on the weight of the hydrocracked base oil).

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Table I

| 5  | Example | Hydrocracked<br>base oil | Aromatic<br>extract |    | Hydrotreated<br>aromatic<br>extract |    | Haze<br>(days) | Sludge<br>(days) | 5  |
|----|---------|--------------------------|---------------------|----|-------------------------------------|----|----------------|------------------|----|
|    |         |                          | type                | %w | type                                | %w |                |                  |    |
|    | (a)     | A                        | -                   | -  | -                                   | -  | 2              | 3                |    |
|    | (b)     | A                        | (1)                 | 2  | -                                   | -  | 5              | 5.5              |    |
| 10 | 1       | A                        | -                   | -  | A                                   | 2  | 7              | 10               | 10 |
|    | (c)     | A                        | (1)                 | 5  | -                                   | -  | (a)            | (a)              |    |
|    | 2       | A                        | -                   | -  | A                                   | 5  | 16             | 20               |    |
|    | (d)     | B                        | -                   | -  | -                                   | -  | 1              | 2                |    |
| 15 | (e)     | B                        | (1)                 | 2  | -                                   | -  | 2.5            | 3                | 15 |
|    | 3       | B                        | -                   | -  | A                                   | 2  | 3.5            | 5.5              |    |
|    | 4       | B                        | -                   | -  | B                                   | 2  | 3              | 5                |    |
|    | 5       | B                        | -                   | -  | C                                   | 2  | 3              | 5                |    |
| 20 | (f)     | B                        | (1)                 | 5  | -                                   | -  | (a)            | (a)              | 20 |
|    | 6       | B                        | -                   | -  | A                                   | 5  | 11             | 14               |    |
|    | 7       | B                        | -                   | -  | B                                   | 5  | 4              | 7                |    |
|    | 8       | B                        | -                   | -  | C                                   | 5  | 3              | 5                |    |
| 25 | (g)     | A                        | (2)                 | 5  | -                                   | -  | 2              | 2                | 25 |
|    | 9       | A                        | -                   | -  | D                                   | 5  | 6              | 10               |    |

(a) too dark for observation after short exposure to light

30 **EXAMPLE 10**

A high viscosity index base oil composition was prepared by adding 5 %w of the aromatic extract (1) described in Examples 1 to 9 to a hydrocracked base oil. The hydrocracked base oil was obtained by hydrocracking a vacuum distillate, having a V.I. of about 42, of a paraffinic crude oil. The hydrocracked base oil had a V.I. of 97 and a viscosity of 9.4 centistokes at 210°F (the V.I. and viscosity of the hydrocracked base oil were determined on dewaxed samples).

The base oil composition was then hydrofinished at a temperature of 300°C, a space velocity of 1.0 kg feed per litre of catalyst per hour and a pressure of 155 bars.

The base oil composition so prepared was then distilled to remove components having a boiling point of below about 400°C and was then dewaxed with a mixture (50/50) of MEK and toluene. The V.I. of the resultant composition was 91.

The base oil composition obtained was then subjected to the daylight stability test described above. The time taken for sludge formation to occur was 38 days.

For comparative purposes a base oil was prepared in a similar manner to the above except that no extract was added to the hydrocracked base oil before the hydrofinishing step. The base oil has a V.I. of 97 and a viscosity of 9.4 centistokes at 210°F. Sludge formation occurred after 4 days.

## WHAT WE CLAIM IS:-

1. A base oil composition comprising  
(a) a hydrocracked base oil (as defined hereinbefore), and  
(b) from 0.01 to 20 %w, based on weight of (a), of a hydrotreated extract of a vacuum distillate or of a deasphalted vacuum residue (all as defined hereinbefore).

2. A base oil composition as claimed in claim 1, wherein component (a) is a hydrocracked and hydrofinished base oil.

3. A base oil composition as claimed in claim 1 or claim 2, prepared by mixing components (a) and (b).

4. A base oil composition as claimed in claim 3 wherein component (a) and/or component (b) are distilled and/or dewaxed before they are mixed or wherein the mixture of component (a) and (b) is distilled and/or dewaxed.

5. A base oil composition as claimed in claim 2, prepared by mixing a hydrocracked base oil with an extract of a vacuum distillate or an extract of a deasphalted vacuum residue and hydrogenating the mixture so as to hydrotreat simultaneously the hydrocracked base oil and the extract of the vacuum distillate or the extract of the deasphalted vacuum residue.

6. A base oil composition as claimed in claim 5, wherein the hydrogenated mixture is distilled and/or dewaxed.



Table I

| 5  | Example | Hydrocracked<br>base oil | Aromatic<br>extract |    | Hydrotreated<br>aromatic<br>extract |    | Haze<br>(days) | Sludge<br>(days) | 5  |
|----|---------|--------------------------|---------------------|----|-------------------------------------|----|----------------|------------------|----|
|    |         |                          | type                | %w | type                                | %w |                |                  |    |
|    | (a)     | A                        | -                   | -  | -                                   | -  | 2              | 3                |    |
| 10 | (b)     | A                        | (1)                 | 2  | -                                   | -  | 5              | 5.5              |    |
|    | 1       | A                        | -                   | -  | A                                   | 2  | 7              | 10               | 10 |
|    | (c)     | A                        | (1)                 | 5  | -                                   | -  | (a)            | (a)              |    |
|    | 2       | A                        | -                   | -  | A                                   | 5  | 16             | 20               |    |
| 15 | (d)     | B                        | -                   | -  | -                                   | -  | 1              | 2                |    |
|    | (e)     | B                        | (1)                 | 2  | -                                   | -  | 2.5            | 3                | 15 |
|    | 3       | B                        | -                   | -  | A                                   | 2  | 3.5            | 5.5              |    |
|    | 4       | B                        | -                   | -  | B                                   | 2  | 3              | 5                |    |
|    | 5       | B                        | -                   | -  | C                                   | 2  | 3              | 5                |    |
| 20 | (f)     | B                        | (1)                 | 5  | -                                   | -  | (a)            | (a)              | 20 |
|    | 6       | B                        | -                   | -  | A                                   | 5  | 11             | 14               |    |
|    | 7       | B                        | -                   | -  | B                                   | 5  | 4              | 7                |    |
|    | 8       | B                        | -                   | -  | C                                   | 5  | 3              | 5                |    |
| 25 | (g)     | A                        | (2)                 | 5  | -                                   | -  | 2              | 2                | 25 |
|    | 9       | A                        | -                   | -  | D                                   | 5  | 6              | 10               |    |

(a) too dark for observation after short exposure to light

### 30 EXAMPLE 10

30 A high viscosity index base oil composition was prepared by adding 5 %w of the aromatic  
extract (1) described in Examples 1 to 9 to a hydrocracked base oil. The hydrocracked base  
oil was obtained by hydrocracking a vacuum distillate, having a V.I. of about 42, of a  
35 paraffinic crude oil. The hydrocracked base oil had a V.I. of 97 and a viscosity of 9.4  
centistokes at 210°F (the V.I. and viscosity of the hydrocracked base oil were determined on  
dewaxed samples).

The base oil composition was then hydrofinished at a temperature of 300°C, a space  
velocity of 1.0 kg feed per litre of catalyst per hour and a pressure of 155 bars.

40 The base oil composition so prepared was then distilled to remove components having a  
boiling point of below about 400°C and was then dewaxed with a mixture (50/50) of MEK  
and toluene. The V.I. of the resultant composition was 91.

The base oil composition obtained was then subjected to the daylight stability test  
described above. The time taken for sludge formation to occur was 38 days.

45 For comparative purposes a base oil was prepared in a similar manner to the above except  
that no extract was added to the hydrocracked base oil before the hydrofinishing step. The  
base oil has a V.I. of 97 and a viscosity of 9.4 centistokes at 210°F. Sludge formation occurred  
after 4 days.

#### WHAT WE CLAIM IS:-

50 1. A base oil composition comprising  
(a) a hydrocracked base oil (as defined hereinbefore), and  
(b) from 0.01 to 20 %w, based on weight of (a), of a hydrotreated extract of a vacuum  
distillate or of a deasphalted vacuum residue (all as defined hereinbefore).

2. A base oil composition as claimed in claim 1, wherein component (a) is a hydrocracked  
and hydrofinished base oil.

55 3. A base oil composition as claimed in claim 1 or claim 2, prepared by mixing compo-  
nents (a) and (b).

4. A base oil composition as claimed in claim 3 wherein component (a) and/or compo-  
nent (b) are distilled and/or dewaxed before they are mixed or wherein the mixture of  
component (a) and (b) is distilled and/or dewaxed.

60 5. A base oil composition as claimed in claim 2, prepared by mixing a hydrocracked base  
oil with an extract of a vacuum distillate or an extract of a deasphalted vacuum residue and  
hydrogenating the mixture so as to hydrotreat simultaneously the hydrocracked base oil and  
the extract of the vacuum distillate or the extract of the deasphalted vacuum residue.

65 6. A base oil composition as claimed in claim 5, wherein the hydrogenated mixture is  
distilled and/or dewaxed.

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7. A base oil composition as claimed in any one of claims 1 to 6, wherein the component (b) is present in an amount of from 0.1 to 10 %w, based on weight of component (a).

8. A base oil composition as claimed in any one of claims 1 to 7, having a viscosity index of at least 90.

5 9. A base oil composition as claimed in any one of claims 1 to 8, comprising as additional additive, a conventional lubricating oil additive. 5

10. A base oil composition as claimed in claim 1, substantially as hereinbefore described with reference to the Examples.

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