

PATENT SPECIFICATION

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- (21) Application No. 26880/79 (22) Filed 23 Jun. 1976
(62) Divided Out of No. 1572793
(23) Complete Specification Filed 14 Dec. 1976
(44) Complete Specification Published 6 Aug. 1980
(51) INT. CL.³ C10M 1/04
(52) Index at Acceptance
CSE TH
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(19)



(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 base 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 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 feedstocks, 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) or a hydrofinished, non-solvent extracted vacuum distillate or hydrofinished, non-solvent extracted 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 15 for distillate base oils and by at least 10 for residual base oils as a result of the hydrogenation treatment. The term "hydrofinished vacuum distillate or hydrofinished deasphalted vacuum residue" as used herein means a vacuum distillate or deasphalted vacuum residue which has been hydrogenated under such conditions that the V.I. of the distillate does not increase by more than 15 units and that the V.I. of the residue does not increase by more than 10 units, as

a result of the hydrogenation treatment.

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 vacuum distillates or deasphalted vacuum residues i.e. deasphalted residues of vacuum distillations, from which the hydrofinished distillates or residues are obtained, are suitably derived from paraffinic crude oils. The hydrofinishing conditions are such that little or no structural alteration of the feedstocks occurs. Usually the distillates and residues are hydrofinished at temperatures from 200 to 350°C, pressures of from 30 to 200 bars and space velocities between 0.1 and 2.0 kg feed per litre of catalyst per hour using catalysts of the same type as described above for the preparation of hydrocracked base oils. The hydrofinished distillates for residues may be subjected to a distillation step in order to remove the more volatile components therefrom. For example, the volatile material boiling below a temperature in the range from 350 to 550°C may be removed before the hydrofinished distillates or residues are mixed with the hydrocracked base oil. The hydrofinished distillates or residues may also be subjected to a dewaxing step but, as mentioned hereinbefore, are not subjected to a solvent extraction step. Mixtures of these hydrofinished distillates and hydrofinished residues may also be used.

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 under substantially the same conditions as described above for the production of hydrofinished distillates or residues.

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 hydrofinished vacuum distillate, or the hydrofinished 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 a vacuum distillate or deasphalted vacuum residue and hydrogenating the mixture so as to hydrofinish simultaneously the hydrocracked base oil and 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. Usually the components boiling below a temperature in the range from 200 to 550°C are removed.

Suitably the base oil compositions, which are suitably high viscosity index base oil compositions, comprise from 0.1 to 10 %w of the hydrofinished 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. tetrabutylidiphenylquinone).

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.

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EXAMPLE 1

A base oil composition was prepared by adding 5 %w of a non-solvent extracted deasphaltered vacuum residue to a hydrocracked base oil. The deasphaltered vacuum residue was obtained from a paraffinic crude oil and had a V.I. of 82 and a viscosity of 56.4 centistokes at 210°F and contained about 35 %w of aromatics. 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 baseoil had a V.I. of 97 and a viscosity of 9.4 centistokes at 210°F. (The V.I.'s and viscosities of the deasphaltered vacuum residue and 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 150 bars.

The base oil composition so prepared was then distilled to remove components having a boiling point below 400°C and was then dewaxed with a mixture (50/50) of MEK and toluene. The V.I. of the resultant composition was 96 indicating that substantially no increase in V.I. has taken place during the hydrofinishing step.

The base oil composition obtained was then subjected to an artificial daylight stability test which comprised irradiating, by means of two 40W 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 sludge formation to occur was 9 days.

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

EXAMPLES 2 to 4

High viscosity index base oil compositions were prepared from the following components. The ratio of components are given in Table I.

Hydrocracked base oil:- obtained by hydrocracking, hydrofinishing, distilling and dewaxing a vacuum distillate, having a V.I. of about 42, of a paraffinic crude oil. The hydrocracked and hydrofinished base oil had a V.I. of about 97 and a viscosity of 9.4 at 210°F.

Fraction (1): A non-solvent extracted deasphaltered vacuum residue derived from a paraffinic crude oil. The residue was dewaxed with a mixture (50/50) of MEK and toluene. The residue had a V.I. of 82 and a viscosity of 56.4 centistokes at 210°F.

Hydrofinished fraction A: Prepared by hydrofinishing fraction (1) at a temperature of 300°C, a space velocity of 1.0 kg feed per litre of catalyst per hour and a pressure of 150 bars. The hydro-finished fraction was then distilled to remove components having a boiling point below about 510°C and was then dewaxed with a mixture (50/50) of MEK and toluene. The V.I. of the resultant hydrofinished fractions was 84.

Fraction (2): A non-solvent extracted vacuum distillate (boiling point 350-530°C) derived from a paraffinic crude oil. The distillate was dewaxed with a mixture (50/50) of MEK and toluene. The distillate had a V.I. of 32 and a viscosity of 23.1 centistokes at 210°F.

Hydrofinished fraction B: Prepared by hydrofinishing fraction (2) at a temperature of 320°C, a space velocity of 1.0 kg feed per litre catalyst per hour and a pressure of 155 bars. The hydrofinished fraction was then distilled to remove components having a boiling point below about 400°C and was then dewaxed with a mixture (50/50) of MEK and toluene. The V.I. of the resultant hydrofinished fraction was 40.

The compositions were subjected to the artificial daylight stability test described above. The results are given in Table I. Example (a) gives the test result for the hydrocracked and hydrofinished base oil itself. Examples (b) and (c) give the test results for mixtures of the hydrocracked and hydrofinished base oil with the unhydro-treated fractions (1) and (2). (The percentages by weight are based on the weight of the hydrocracked base oil.)

Table 1

Example	Fraction		Hydrofinished fraction		Haze (days)	Sludge (days)	
	type	%w	type	%w			
5	(a)	-	-	-	3	4	5
	(b)	(1)	-	-	-	11	
	2	-	A	5	-	24	
10	3	-	A	9	-	26*	10
	(c)	(2)	-	-	2	2	
	4	-	B	5	-	8	

*test stopped after 26 days

EXAMPLE 5

The compositions of Examples (a), (b) and 2 were subjected to a standard oxidation test which comprised blowing oxygen through the compositions at a temperature of 160°C for 168 hours. At the end of the test the amount of lacquer or sludge formed was determined. The results are given in Table II.

Table II

Example	Composition of Example No.	Total sludge + lacquer	
(d)	(a)	3.3	25
(e)	(b)	0.65	
5	2	0.25	

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 hydrofinished, non-solvent extracted vacuum distillate or hydrofinished, non-solvent extracted 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 a vacuum distillate or deasphalted vacuum residue and hydrogenating the mixture so as to hydrofinish simultaneously the hydrocracked base oil and the vacuum distillate or the deasphalted vacuum residue.
6. A base oil composition as claimed in claim 5, wherein the hydrogenated mixture is distilled and/or dewaxed.
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.
9. A base oil composition as claimed in any one of claims 1 to 8, comprising as additional additive, a conventional lubricating oil additive.
10. A base oil composition as claimed in claim 1, substantially as hereinbefore described with reference to the Examples.

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6. A base oil composition as claimed in claim 5, wherein the hydrogenated mixture is distilled and/or dewaxed.
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.
9. A base oil composition as claimed in any one of claims 1 to 8, comprising as additional additive, a conventional lubricating oil additive.
10. A base oil composition as claimed in claim 1, substantially as hereinbefore described with reference to the Examples.

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