

LUBRICATING BASE OIL COMPOSITIONS

The invention relates to lubricating base oil compositions with improved stability.

To be suitable for use as lubricating base oil, an oil should have, in addition to a certain minimum viscosity, a certain minimum viscosity index. Fractions from crude mineral oil having a sufficiently high viscosity for use as lubricating base oil, such as vacuum distillates and deasphalted vacuum residues, have, as a rule, a very low viscosity index, which is caused by the presence in these oils of a considerable amount of polyaromatics. A strong reduction of the polyaromatics content of the oils gives oils with a sufficiently high viscosity index to make them suitable for use as lubricating base oil. The desired reduction of the polyaromatics content may, in principle, be carried out in two different ways. The oil may be extracted with a selective solvent for polyaromatics, which produces a raffinate with the desired high viscosity index. Or the oil may be subjected to a catalytic hydrotreatment under such conditions that, among other things, polyaromatics are converted into compounds with a high viscosity index. The two treatments may also be combined. The starting material may first be subjected to a solvent extraction and the raffinate obtained may subsequently be subjected to a catalytic hydrotreatment. It is also possible to subject the starting material to a catalytic hydrotreatment first and then to subject the hydrotreated product to solvent extraction.

Processes for the preparation of lubricating base oils, in which polyaromatics are converted into valuable lubricating oil components by a catalytic hydrotreatment are to be preferred to processes in which the polyaromatics are removed from the

oils by solvent extraction, since the former processes give a higher yield of lubricating base oils and the increase in the viscosity index is greater. These advantages also apply to the processes in which a combination of catalytic hydrotreatment and solvent extraction is used to reduce the polyaromatics content, the advantage being greater, of course, according as a greater part of the polyaromatics is converted by means of a catalytic hydrotreatment. A drawback of the preparation of lubricating base oils from vacuum distillates and deasphalted vacuum residues by means of a catalytic hydrotreatment is that the catalytic hydrotreatment often has an unfavourable influence on the oxidation stability of the lubricating base oil prepared. This is connected with the removal of sulphur compounds from the oil occurring simultaneously with the conversion of the polyaromatics. Accordingly if the catalytic hydrotreatment is carried out under severer conditions in order to convert a greater part of the polyaromatics into valuable lubricating oil components, a lubricating base oil is obtained with a lower oxidation stability. As a rule, it is true that, if the catalytic hydrotreatment is carried out under such conditions that it results in a reduction of the sulphur content of the oil of more than 90% (for the sake of brevity in this patent application further designated as "severe catalytic hydrotreatment"), a lubricating base oil is obtained with an unacceptably low oxidation stability for practical use. This rule holds both for the preparation of lubricating base oils exclusively by a severe catalytic hydrotreatment and for the preparation of lubricating base oils by a combination of a severe catalytic hydrotreatment and a solvent extraction. In this patent application the reduction of the sulphur content is meant to denote:

$$\frac{\%w \text{ S in feed} - \%w \text{ S in product}}{\%w \text{ S in the feed}} \times 100\%$$

where the %w S in product relates to the sulphur content of the hydrotreated product after components boiling below the initial boiling point of the feed have been boiled off.

British patent specification 2,024,852 relates to the improvement of the oxidation stability of lubricating base oils prepared from a vacuum distillate or deasphalted vacuum residue, using a severe catalytic hydrotreatment in combination with solvent extraction. It was found in this investigation that the oxidation stability of these lubricating base oils can be considerably improved by adding to them 0.01-20%w of an oil which has been prepared by applying to a vacuum distillate or deasphalted vacuum residue either solvent extraction or a mild catalytic hydrotreatment. To make a distinction between the severe catalytic hydrotreatment used in the present preparation of lubricating base oil, in which a sulphur content reduction of more than 90% takes place, a mild catalytic hydrotreatment is now defined as a treatment in which a sulphur content reduction of less than 75% takes place. Although a considerable increase of the oxidation stability of the lubricating base oils can be obtained when the above-mentioned oils are used as additives, there remains a need for a further improvement of this property. A drawback of the application of the oils prepared either by solvent extraction or by mild catalytic hydrotreatment is that they sometimes have an adverse influence on the daylight stability of the lubricating base oil to which they are added.

Continued investigation concerning this subject by the Applicant has now shown that by using a combination of a mild hydrotreatment and a solvent extraction oils can be prepared which give a far greater improvement of the oxidation stability when added to the above-mentioned lubricating base oils than the aforementioned oils, in the preparation of which only one of these treatments was applied. It was further found that use of these oils as additives causes a considerable increase in the daylight stability of the lubricating base oils.

The present patent application therefore relates to a lubricating base oil composition containing:

- (a) a lubricating base oil prepared from a vacuum distillate, a deasphalted vacuum residue or a mixture thereof, by applying to it a severe catalytic hydrotreatment, which catalytic hydrotreatment has optionally been carried out in combination with a solvent extraction, and
- (b) 0.01-20%w, calculated on the weight of the oil mentioned under (a), of an oil prepared from a vacuum distillate, a deasphalted vacuum residue or a mixture thereof, by applying to it a combination of a mild catalytic hydrotreatment and a solvent extraction.

Although the lubricating base oils and the oils added to the lubricating base oils may have been obtained from a mixture of a vacuum distillate and a deasphalted vacuum residue, in the formation of the lubricating base oil compositions according to the invention preference is given to lubricating base oils and additive oils prepared either from a vacuum distillate, or from a deasphalted vacuum residue. If the lubricating base oil has been prepared from a vacuum distillate, oils may be added to it which have been prepared from a vacuum distillate or from a deasphalted vacuum residue. If the lubricating base oil has been prepared from a deasphalted vacuum residue, it is preferred, with a view to the volatility of the ultimate lubricating base oil composition, to add oils which have also been prepared from a deasphalted vacuum residue.

The lubricating base oils used in the compositions according to the invention may have been prepared either by means of a severe catalytic hydrotreatment, or by means of a combination of a severe catalytic hydrotreatment and a solvent extraction. If the lubricating base oils are prepared without using solvent extraction, a second catalytic hydrotreatment is often carried out (designated: hydrofinishing) after the severe catalytic hydrotreatment to improve the quality of the oil. If

the lubricating base oils are prepared using a combination of a severe catalytic hydrotreatment and a solvent extraction, the sequence of these treatment steps is free. A solvent extraction may first be applied to the starting material, followed by a severe catalytic hydrotreatment of the raffinate, or a severe catalytic hydrotreatment may first be applied to the starting material, followed by a solvent extraction of the hydrotreated product. If the lubricating base oils are prepared using a combination of a severe catalytic hydrotreatment and a solvent extraction, the preferred sequence is the one where the starting material is first subjected to solvent extraction.

The oils added to the lubricating base oils are prepared using a combination of a solvent extraction and a mild catalytic hydrotreatment, the sequence of these treatment steps being free. In the preparation of these oils it is preferred first to apply solvent extraction to the starting material and then a mild catalytic hydrotreatment to the raffinate obtained.

If in the preparation of the lubricating base oil use is made of a combination of solvent extraction and a severe catalytic hydrotreatment, the apparatus in which the solvent extraction for the preparation of the lubricating base oil is carried out, may very suitably be used for the solvent extraction for the preparation of the additive oil as well. For instance, on the basis of this principle lubricating base oil compositions according to the invention may be prepared by applying solvent extraction to a starting material, dividing the raffinate obtained into two portions, applying to one portion a severe catalytic hydrotreatment and to the other portion a mild catalytic hydrotreatment and, finally, combining the two hydrotreated products. On the basis of this principle it is also possible to prepare lubricating base oil compositions according to the invention by dividing a starting material into two portions, applying to one portion a severe catalytic hydrotreatment and to the other portion a mild catalytic hydrotreatment, combining the two

hydrotreated products, and, finally, applying solvent extraction to the mixture.

If in the preparation of the lubricating base oil use is made of a severe catalytic hydrotreatment followed by a hydrofinishing, in which the conditions under which the hydrofinishing is carried out are such that they are in agreement with those required for the mild catalytic hydrotreatment for the preparation of the additive oil, the apparatus in which the hydrofinishing for the preparation of the lubricating base oil is carried out, may very suitably also be used for the mild catalytic hydrotreatment for the preparation of the additive oil. On the basis of this principle it is possible, for instance, to prepare lubricating base oil compositions according to the invention by dividing a starting material into two portions, applying to one portion a severe catalytic hydrotreatment and to the other portion solvent extraction, combining the hydrotreated product and the raffinate of the solvent extraction, and, finally, applying a mild catalytic hydrotreatment to the mixture.

The lubricating base oils used in the lubricating base oil compositions according to the invention have been prepared starting from a vacuum distillate or deasphalted vacuum residue by applying to these products a severe catalytic hydrotreatment, if desired in combination with a solvent extraction. In these treatments it is generally intended to achieve a reduction of the polyaromatics content of more than 75%. In this patent application the reduction of the polyaromatics (PA) content is meant to denote:

$$\frac{\text{mmol}/100 \text{ g PA in feed} - \text{mmol}/100 \text{ g PA in end product}}{\text{mmol}/100 \text{ g PA in feed}} \times 100\%$$

where mmol/100 g PA in end product relates to the polyaromatics content of the end product after components boiling below the initial boiling point of the feed have been distilled off. As a rule, the severe catalytic hydrotreatment is carried out at a temperature of 340-500°C, a pressure of 60-200 bar and a space velocity of 0.1-2 kg.l⁻¹.h⁻¹. Suitable catalysts for carrying

out the severe catalytic hydrotreatment are catalysts containing one or more metals with hydrogenation activity on a carrier.

Examples of suitable metals are: iron, nickel, cobalt, chromium, tungsten, molybdenum, platinum and copper, in particular com-

- 5 combinations of these metals such as nickel-molybdenum, cobalt-molybdenum and nickel-tungsten. Suitable carrier materials are: silica, alumina, zirconia and magnesia and combinations thereof such as silica-alumina. If desired, the catalysts may contain promoters such as halogen, phosphorus or boron.

- 10 The oils added to the lubricating base oils in the formation of the lubricating base oil compositions according to the invention have been prepared from a vacuum distillate or deasphalted vacuum residue by applying to these products a combination of a mild catalytic hydrotreatment and a solvent ex-
- 15 traction. As a rule, the mild catalytic hydrotreatment is carried out at a temperature of 200-340°C, a pressure of 30-200 bar and a space velocity of 0.1-2 kg.l⁻¹.h⁻¹. Suitable catalysts for the mild catalytic hydrotreatment are, in principle, the same catalysts as may be used in the severe catalytic hydrotreatment.

- 20 The solvent extraction that has to be used in the preparation of the oils to be added to the lubricating base oils and which may optionally be used in the preparation of the lubricating base oils, is a known technique: suitable solvents are phenol, furfural, N-methyl-pyrrolidone and sulphur dioxide. In the
- 25 extraction a raffinate is obtained which is poor in polyaromatics and an extract rich in polyaromatics.

- In the preparation of both the lubricating base oils and the additive oils it is preferred to start from vacuum distillates and deasphalted vacuum residues originating from paraffinic crude
- 30 oils. With a view to the volatility of the lubricating base oil compositions according to the invention, light components formed in the catalytic hydrotreatment of the lubricating base oils and the additive oils are removed by distillation. Any heavy paraffins present in the lubricating base oils and the additive oils may,

with a view to the pour point of the lubricating base oil compositions, be removed by dewaxing. Both the distillation and the dewaxing may be applied to the lubricating base oils and the additive oils separately, or to their mixtures.

5 The amount of oil that should be added to the lubricating base oil is at least 0.01 and at most 20%w, calculated on the weight of the lubricating base oil. It is preferred to add 0.1-10%w of the oil, calculated on the weight of the lubricating base oil. The lubricating base oil compositions according to the
10 invention are very suitable for use for the lubrication of internal combustion engines or for use as industrial lubricants. They may contain one or more of the usual additives, such as agents to improve the viscosity index, anti-wear additives, detergents, high-pressure additives, corrosion-inhibiting
15 additives, pour point reducers and other anti-oxidants, such as secondary amines and other stabilizing agents for daylight, such as quinones.

 The invention will now be further explained with reference to the following example. The V.I. values given in the example
20 were all determined on oil samples, the pour point of which had first been reduced to -9°C by dewaxing.

EXAMPLE

 Two lubricating base oils (I and II) and six blend components (1-6) were prepared as follows:

25 Oil I

 The starting material for the preparation of this oil was a vacuum distillate with a sulphur content of 2.66%w, a polyaromatics content of 31 mmol/100 g and a V.I. of 57. The vacuum distillate had been obtained from a paraffinic crude oil from
30 the Middle East. The vacuum distillate was extracted with furfural, which produced a raffinate in a yield of 70%, based on the vacuum distillate. The raffinate had a sulphur content of 1.32%w and a polyaromatics content of 3.4 mmol/100 g and a V.I. of 88. The raffinate was subjected to a severe catalytic

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hydrotreatment at a temperature of 342°C , a pressure of 105 bar, a space velocity of $1.5 \text{ kg.l}^{-1}.\text{h}^{-1}$ and an H_2/oil ratio of 1200 Nl.kg^{-1} and using a fluorine-containing catalyst containing the metal combination nickel-tungsten on alumina as the carrier. Light components boiling below the initial boiling point of the raffinate were removed from the hydrotreated product by distillation. The remaining oil which had been obtained in a yield of 89%, based on the raffinate, had a sulphur content of 0.004%w, a polyaromatics content of 0.34 mmol/100 g and a V.I. of 102. Lubricating base oil I was prepared from this oil by dewaxing to a pour point of -9°C .

Oil II

The starting material for the preparation of this oil was a deasphalted vacuum residue with a sulphur content of 2.70%w, a polyaromatics content of 26 mmol/100 g and a V.I. of 78. The deasphalted vacuum residue had been obtained from a paraffinic crude oil from the Middle East. The deasphalted vacuum residue was subjected to a severe catalytic hydrotreatment at a temperature of 376°C , a pressure of 155 bar, a space velocity of $1.0 \text{ kg.l}^{-1}.\text{h}^{-1}$ and a gas velocity of 1500 Nl.kg^{-1} and using the same catalyst as used in the preparation of oil I. Light components boiling below the initial boiling point of the deasphalted vacuum residue were removed from the hydrotreated product by distillation. The remaining oil which had been obtained in a yield of 73%, based on the deasphalted vacuum residue, had a sulphur content of 0.017%w, a polyaromatics content of 1.6 mmol/100 g and a V.I. of 98. Lubricating base oil II was prepared from this oil by dewaxing to a pour point of -9°C .

Oil 1

This oil was prepared by dewaxing the raffinate obtained as intermediate product in the preparation of oil I to a pour point of -9°C .

Oil 2

This oil was prepared by subjecting the vacuum distillate used in the preparation of oil I to a mild catalytic hydro-treatment at a temperature of 315°C , a pressure of 155 bar, a space velocity of $1.0 \text{ kg.l}^{-1}.\text{h}^{-1}$ and an H_2/oil ratio of 1500 Nl.kg^{-1} and using the same catalyst as used in the preparation of oil I. Light components boiling below the initial boiling point of the vacuum distillate were removed from the hydro-treated product by distillation. The remaining oil showed a sulphur content reduction of 45% with respect to the vacuum distillate. Oil 2 was prepared from this oil by dewaxing to a pour point of -9°C .

Oil 3

This oil was prepared by subjecting the raffinate obtained as the intermediate product in the preparation of oil I to a mild catalytic hydrotreatment at a temperature of 270°C , a pressure of 105 bar, a space velocity of $1.0 \text{ kg.l}^{-1}.\text{h}^{-1}$ and an H_2/oil ratio of 1200 Nl.kg^{-1} and using the same catalyst as used in the preparation of oil I. Light components boiling below the initial boiling point of the raffinate were removed from the hydrotreated product by distillation. The remaining oil showed a sulphur content reduction of 40% with respect to the raffinate. Oil 3 was prepared from this oil by dewaxing to a pour point of -9°C .

Oil 4

This oil was prepared by extracting with furfural the de-asphalted vacuum residue used in the preparation of oil II, which produced a raffinate in a yield of 86%, based on the deasphalted vacuum residue. The raffinate had a sulphur content of 2.26%w, a polyaromatics content of 14 mmol/100 g, and a V.I. of 88. Oil 4 was prepared from this oil by dewaxing to a pour point of -9°C .

Oil 5

This oil was prepared by subjecting the deasphalted vacuum residue used in the preparation of oil II to a mild catalytic hydrotreatment at a temperature of 330°C, a pressure of 155 bar, a space velocity of 1.0 kg.l⁻¹.h⁻¹ and an H₂/oil ratio of 1500 Nl.kg⁻¹ and using the same catalyst as used in the preparation of oil I. Light components boiling below the initial boiling point of the deasphalted vacuum residue were removed from the hydrotreated product by distillation. The remaining oil showed a sulphur content reduction of 60% with respect to the deasphalted vacuum residue. Oil 5 was prepared from this oil by dewaxing to a pour point of -9°C.

Oil 6

This oil was prepared from the same raffinate as that from which oil 4 had been prepared by dewaxing, by subjecting the raffinate to a mild catalytic hydrotreatment at a temperature of 320°C, a pressure of 105 bar, a space velocity of 1.0 kg.l⁻¹.h⁻¹ and an H₂/oil ratio of 1200 Nl.kg⁻¹ and using the same catalyst as used in the preparation of oil I. Light components boiling below the initial boiling point of the raffinate were removed from the hydrotreated product by distillation. The remaining oil showed a sulphur content reduction of 50% with respect to the raffinate. Oil 6 was prepared from this oil by dewaxing to a pour point of -9°C.

Seven lubricating base oil compositions (A-G) were formed by adding a small amount of one of the oils 1-6 to the lubricating base oils I and II. The oxidation stability and the daylight stability of the lubricating base oils I and II and of the lubricating base oil compositions A-G were investigated.

The oxidation stability of the oils was investigated in a test in which air is blown through the oil for 168 hours at a temperature of 160°C and in which at the end of the test the amount of sludge obtained, the acidity and the increase in the viscosity of the oil are determined.

The daylight stability of the oils was investigated in a test in which two fluorescent tubes (Philips TL 40 W/S 7^{RTM}) are used for irradiating Pyrex ASTM test tubes^{RTM} which are normally used for solidifying point tests and which contain 30 g oil
5 and are kept at a temperature of $35 \pm 0.5^{\circ}\text{C}$; this test determines the number of days after which sludge formation occurs.

The composition of the various oils and the results of the oxidation and daylight stability tests are listed in the Table.

TABLE

Experiment No.	Lubricating base oil or lubricating base oil composition No.	Composition of the lubricating base oil composition	Oxidation stability			Daylight stability sludge (days)
			sludge, %w calculated on oil	acidity, mg eq/100 g	viscosity increase %	
1	I	-	11	36	1125	4
2	A	oil I + 5% oil 1	0.4	3	19	2
3	B	oil I + 5% oil 2	0.6	4	25	4
4	C	oil I + 5% oil 3	0.2	3	15	6
5	D	oil I + 2% oil 4	0.4	3	20	5
6	E	oil I + 2% oil 5	0.5	4	22	6
7	F	oil I + 2% oil 6	0.2	3	17	8
8	II	-	-	7	35	> 15
9	G	oil II + 2% oil 6	-	2	9	> 15

Of the lubricating base oil compositions A-G listed in the Table, only the lubricating base oil compositions C, F and G are compositions according to the invention. These compositions were formed by adding to a lubricating base oil a small amount of an oil prepared by a combination of a solvent extraction and a mild catalytic hydrotreatment. The compositions A, B, D and E are outside the scope of the invention and have been included in the patent application for comparison.

Comparison of the experiments 1-4 shows that addition of the oils 1 and 2 to lubricating base oil I causes an improvement of the oxidation stability, which improvement is greatest when oil 1 is used. Use of oil 1 results, however, in a sharp fall in the daylight stability. Use of oil 3 (according to the invention) produces not only an increase in the oxidation stability greater than the one obtained when using oil 1, but also a sharp increase in the daylight stability.

Comparison of the experiments 1 and 5-7 shows that addition of the oils 4 and 5 to base oil I causes both an improvement of the oxidation stability and of the daylight stability. Oil 4 gives the greatest improvement of the oxidation stability and oil 5 gives the greatest improvement of the daylight stability. Use of oil 6 (according to the invention) produces not only an increase in the oxidation stability greater than the one obtained when using oil 4, but also an increase in the daylight stability which is greater than the one obtained when using oil 5.

Comparison of the experiments 1 and 7 shows that oil 6 is very suitable for increasing the oxidation and the daylight stability of a lubricating base oil which has been prepared by applying the combination of a solvent extraction and a severe catalytic hydrotreatment to a vacuum distillate. Comparison of the experiments 8 and 9 shows that oil 6 is also suitable for increasing the oxidation stability of a lubricating base oil prepared by applying exclusively severe catalytic hydrotreatment to a deasphalted vacuum residue.

C L A I M S

1. Lubricating base oil compositions containing:
 - (a) a lubricating base oil prepared from a vacuum distillate, a deasphalted vacuum residue or a mixture thereof, by applying to it a catalytic hydrotreatment under such conditions that a sulphur content reduction of more than 90% is reached (further designated as severe catalytic hydrotreatment), which catalytic hydrotreatment has been carried out, if desired, in combination with a solvent extraction, and
 - (b) 0.01-20%w, calculated on the weight of the oil mentioned under (a), of an oil prepared from a vacuum distillate, a deasphalted vacuum residue or a mixture thereof, by applying to it a combination of a catalytic hydro-treatment and a solvent extraction, which catalytic hydrotreatment has been carried out under such conditions that a sulphur content reduction of less than 75% is reached (further designated as mild catalytic hydro-treatment).
2. Lubricating base oil compositions according to claim 1, characterized in that the oil mentioned under (a) has been prepared from a vacuum distillate or from a deasphalted vacuum residue and in that the oil mentioned under (b) has been prepared from a deasphalted vacuum residue.
3. Lubricating base oil compositions according to claim 1, characterized in that both the oil mentioned under (a) and the oil mentioned under (b) have been prepared from a vacuum distillate.
4. Lubricating base oil compositions according to any one of claims 1-3, characterized in that the oil mentioned under (a) has been prepared by first applying solvent extraction to the starting material and then the severe catalytic hydrotreatment to the raffinate.



5. Lubricating base oil compositions according to any one of claims 1-4, characterized in that the oil mentioned under (b) has been prepared by first applying solvent extraction to the starting material and then the mild catalytic hydrotreatment to the raffinate.
6. Lubricating base oil compositions according to any one of claims 1-5, characterized in that both the oil mentioned under (a) and the oil mentioned under (b) have been prepared from a paraffinic feed.
7. Lubricating base oil compositions according to any one of claims 1-6, characterized in that they contain an oil as mentioned under (b) in an amount of 0.1-10%w, calculated on the weight of the oil mentioned under (a).
8. Lubricating base oil compositions substantially as described hereinbefore and in particular with reference to the compositions C, F and G in the example.
9. A process for the preparation of a lubricating base oil composition according to any one of claims 1-8, characterized in that solvent extraction is applied to a vacuum distillate or to a deasphalted vacuum residue, in that the raffinate obtained is divided into two portions, in that a severe catalytic hydrotreatment is applied to one portion and a mild catalytic hydrotreatment to the other portion and, finally, in that the two hydrotreated products are combined.
10. A process for the preparation of a lubricating base oil composition according to any one of claims 1-8, characterized in that a vacuum distillate or a deasphalted vacuum residue is divided into two portions, in that a severe catalytic hydro-treatment is applied to one portion, and a mild catalytic hydrotreatment to the other portion, in that the two hydro-treated products are combined and, finally, in that solvent extraction is applied to the mixture.



11. A process for the preparation of a lubricating base oil composition according to any one of claims 1-8, characterized in that a vacuum distillate or a deasphalted vacuum residue is divided into two portions, in that a severe catalytic hydro-
5 treatment is applied to one portion and a solvent extraction to the other portion, in that the hydrotreated product and the raffinate of the solvent extraction are combined and, finally, in that a mild catalytic hydrotreatment is applied to the mixture.

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