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(54) PROCESS FOR THE PREPARATION OF LUBRICATING OILS

(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 present invention relates to a process for the preparation of lubricating oils with a viscosity index lower than 90.

Lubricating oils can be classified according to their viscosity index (VI) as oils with a low viscosity index (LVI oils, VI < 30), oils with a medium viscosity index (MVI oils, VI varying between 30 and 90), oils with a high viscosity index (HVI oils, VI varying between 90 and 120) and oils with a very high viscosity index (VHVI oils, VI > 120).

For the preparation of HVI and VHVI oils paraffinic crude oils are used as the feed. MVI and LVI oils are normally prepared from naphthenic crude oils.

In this specification and the appurtenant claims the term "paraffinic crude oils" relates to crude mineral oils containing a considerable proportion of paraffins having a melting point above 15°C.

In this specification the term "naphthenic crude oils" refers to crude mineral oils containing no or hardly any paraffins having a melting point above 15°C.

Since the availability of sufficient quantities of naphthenic crude oils is going to be a problem for a number of oil companies in the near future, it would be attractive if the distillate fractions obtained from naphthenic crude oils and used for the preparation of LVI and MVI lubricating oils could be replaced by other oil fractions.

In areas only having facilities for the preparation of HVI lubricating oil, it would be particularly advantageous if MVI and LVI lubricating oils could be prepared from the HVI feed. It would be especially advantage-

ous if MVI and LVI lubricating oils could be prepared from a paraffinic crude oil without a drop in the yield of HVI lubricating oil prepared from this feed.

The criterion to be met by such an MVI or LVI lubricating oil to be prepared from an HVI lubricating oil feed is that the viscometric, colour and oxidation stability properties should be comparable with those of MVI and LVI lubricating oils prepared entirely from a naphthenic crude oil as the feed.

It has now been found that LVI and MVI lubricating oils that are based entirely on paraffinic base materials can be prepared by subjecting by-products obtained in the preparation of HVI lubricating oils to a catalytic hydrotreatment.

In the preparation of distillate and residual HVI lubricating oils from paraffinic crude oils, which is normally effected in succession by atmospheric distillation, vacuum distillation, deasphalting of the vacuum residue, aromatics extraction of the vacuum distillates and of the deasphalted vacuum residue and dewaxing of the extracted fractions, there are among the by-products aromatic extracts which are only of little value and are as a rule used as fuel components. These aromatic extracts, prepared from distillate fractions and deasphalted residual lubricating oil fractions and generally having a relatively low VI are, as far as their viscosity properties are concerned, suitable for use as MVI and LVI oils. However, the aromatic extracts generally have an unattractive colour as well as a poor oxidation stability. Consequently, they are not used as lubricating oil in cases where a light colour and/or a good oxidation stability are desirable.

In an investigation carried out by the Applicants concerning the preparation of LVI and MVI oils it has been found that the colour as well as the oxidation stability of aromatic extracts from both distillate fractions and deasphalted residual lubricating oil fractions can be improved by contacting these extracts at elevated temperature and pressure and in the

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presence of hydrogen with a catalyst comprising one or more metals of Groups VIB, VIIB and VIII or sulphides or oxides thereof supported on a carrier comprising one or more oxides of elements of Groups II, III and IV, which catalysts may comprise promoters such as phosphorus or boron and a halogen, such as chlorine or fluorine.

It has been found that the extent to which improvements in colour and in oxidation stability occur and the yield of a product that can be used as LVI or MVI lubricating oil greatly depends on the type and quantity of metals and halogen present on the carrier and on the type of carrier and its properties. The reaction conditions under which the catalytic hydrotreatment is carried out also play an important part in this connection.

If the preparation of LVI and MVI oils by catalytic hydro-treatment of aromatic extracts from lubricating oil fractions is taken to be economically attractive only when it goes with a great improvement in colour and oxidation stability, combined with a high yield of product, only a small group of the above-mentioned catalysts proves to be eligible, and that only when they are used under specific conditions. The notions great improvement in colour and in oxidation stability, as well as a high yield can, depending on the starting material chosen, be further quantified as follows.

For the catalytic hydrotreatment of an aromatic extract from a distillate lubricating oil fraction the requirements are that from an extract being darker than 8 colour and producing more than 6 % w of sludge in a standard oxidation test, more than 85 % w of an oil is obtained having an initial boiling point that is 100°C below the initial boiling point of the feed, which oil is 3 colour or lighter and produces less than 3 % w of sludge in the standard oxidation test.

For the catalytic hydrotreatment of an aromatic extract from a deasphalted residual lubricating oil fraction the requirements are that from an extract being darker than 8 colour and producing more than 0.5 % w of sludge in the standard oxidation test, more than 85 % w of an oil is obtained having an initial boiling point that is 200°C below the initial boiling point of the feed, which oil is 3 colour or lighter and produces less than 0.3 % w of sludge in the standard oxidation test.

The colour numbers mentioned in this patent application have been determined according to ASTM-D-1500. The standard oxidation test is a modified version of IP 48/67, in which, instead of a temperature of 200°C and a testing time of 12 hours, a temperature of 130°C and a testing time of 24 hours were applied and in which the test tube contained a copper wire and an iron

wire, each 40 cm long and 1.5 mm in diameter.

It has now been found that these requirements can be met if for the catalytic hydro-treatment use is made of the catalysts that are the subjects of United Kingdom Patent 1,493,620 and of Netherlands patent applications No. 7,506,416 and No. 7,602,603, provided that they are used at a temperature above 350°C, a hydrogen partial pressure above 100 bar and a space velocity below 1.5 kg.l⁻¹.h⁻¹. The catalysts that are the subjects of the two above-mentioned Netherlands patent applications in the name of the Applicants, are fluorine-containing catalysts containing either nickel and/or cobalt and, in addition, molybdenum, or nickel and tungsten on alumina as the carrier, which catalysts have a compacted bulk density of less than 0.8 g/ml, comprise at least 3 parts by weight of nickel and/or cobalt, at least 10 parts by weight of molybdenum and/or at least 20 parts by weight of tungsten, respectively, per 100 parts by weight of carrier, and have been prepared from an alumina hydrogel from which, by drying and calcining, a xerogel can be obtained having a compacted bulk density of less than 0.8 g/ml:

1. If the pore volume quotient of the said xerogel is at least 0.5, the preparation of the catalyst is effected, either
 - a) by drying and calcining the alumina hydrogel, incorporation of nickel and tungsten into the xerogel and once more drying and calcining the composition, or
 - b) by incorporation of the metals into the alumina hydrogel, and drying and calcining the composition.
2. If the pore volume quotient of the said xerogel is less than 0.5, the preparation of the catalyst is effected, either
 - a) by incorporation of at least part of the fluorine into the alumina hydrogel, and drying and calcining the composition, incorporation of nickel and tungsten into the xerogel and once more drying and calcining the composition, or
 - b) by incorporation of the metals and at least part of the fluorine into the alumina hydrogel, and drying and calcining the composition, with the proviso in both (a) and (b) that sufficient fluorine should be incorporated into the alumina hydrogen to produce from this fluorine-containing alumina hydrogel, by drying and calcining, a xerogel having a pore volume quotient of at least 0.5. For a further description of the pore volume quotient reference is made to the above-mentioned United Kingdom patent and Netherlands patent applications.

For the sake of brevity, in the present patent application the catalyst preparation in which the metals are incorporated into the hydrogel will hereinafter be referred to as the hydrogel route and the one in which the metals are incorporated into the xerogel as the xerogel route.

The present patent application therefore relates to a process for the preparation of lubricating oils having a viscosity index lower than 90 by catalytic hydrotreatment of an aromatic extract from a distillate or deasphalted residual lubricating oil fraction using the catalysts mentioned hereinbefore, at a temperature above 350°C, a hydrogen partial pressure above 100 bar and a space velocity below 1.5 kg.l⁻¹.h⁻¹.

If in the process according to the invention a catalyst is employed comprising nickel and tungsten and which has been prepared by the xerogel route, preference is given to a catalyst comprising 3—12 parts by weight of nickel and 20—75 parts by weight of tungsten per 100 parts by weight of alumina and in particular to such a catalyst in which the nickel-to-tungsten weight ratio is between 1:5 and 1:7.

If in the process according to the invention a catalyst is employed comprising nickel and tungsten and which has been prepared by the hydrogel route, preference is given to a catalyst comprising 25—50 parts by weight of nickel and 50—80 parts by weight of tungsten per 100 parts by weight of alumina and in particular to such a catalyst in which the nickel-to-tungsten weight ratio is between 1:1.5 and 1:5.

If in the process according to the invention a catalyst is employed comprising nickel and/or cobalt and, in addition, molybdenum, preference is given to a catalyst comprising 25—80 parts by weight of nickel and/or cobalt and 50—80 parts by weight of molybdenum per 100 parts by weight of alumina and in particular to such a catalyst in which the weight ratio between nickel and/or cobalt on the one hand and molybdenum on the other is between 1:1 and 1:5.

The quantity of fluorine present in the catalysts used according to the invention is preferably 0.5—10 parts by weight per 100 parts by weight of alumina, if they have been prepared by the xerogel route, and 10—25 parts by weight per 100 parts by weight of alumina, if they have been prepared by the hydrogel route. For a further description of the way in which the present catalysts can be prepared reference is made to the aforementioned Netherlands patent applications.

The aromatic extracts which in the process according to the invention are employed as the starting material may have been obtained either by extraction of lubricating oil fractions originating from paraffinic crude oils or by extraction of lubricating oil fractions originating from naphthenic crude oils. As explained

hereinbefore the invention is especially important for the preparation of LVI and MVI lubricating oils from aromatic extracts obtained by extraction of lubricating oil fractions originating from paraffinic crude oil as the starting material.

In the process according to the invention an aromatic extract from a distillate lubricating oil fraction or an aromatic extract from a deasphalted residual lubricating oil fraction is used as the starting material. Eligible solvents are, inter alia, furfural, phenol and sulphur dioxide. Furfural is preferred for this purpose. If the extraction is applied to a residual lubricating oil fraction, asphalt should first be removed from it. Deasphalting can very suitably be effected by contacting the residual lubricating oil fraction at elevated temperature and pressure with an excess of a lower hydrocarbon such as propane, butane, pentene or a mixture thereof. Propane is preferred for this purpose.

According to the invention the catalyst hydrotreating of the aromatic extracts has to be carried out at a temperature above 350°C, a hydrogen partial pressure above 100 bar and a space velocity below 1.5 kg.l⁻¹.h⁻¹. The catalytic hydrotreatment is preferably carried out at a temperature below 425°C and in particular below 400°C, a hydrogen partial pressure below 200 bar and in particular below 175 bar, a space velocity above 0.5 kg.l⁻¹.h⁻¹ and a hydrogen/oil ratio of from 250 to 2500 NL.kg⁻¹ and in particular of from 500 to 2000 NL.kg⁻¹.

Aromatic extracts from lubricating oil fractions originating from paraffinic crude oils may have a relatively high pour point. If the pour point of a given aromatic extract is too high in view of the use of the LVI or MVI lubricating oil to be prepared from this aromatic extract, this pour point has to be reduced. This may be done by dewaxing the aromatic extract or the LVI or MVI lubricating oil prepared from it by catalytic hydrotreatment. A very suitable method for dewaxing an aromatic extract with a high pour point or an LVI or MVI lubricating oil prepared from it by catalytic hydrotreatment is cooling down the oil concerned in the presence of a mixture of methyl ethyl ketone and toluene. A reduction of the pour point of LVI and MVI lubricating oils prepared according to the invention may also be realised by the addition of a pour point reducer. Examples of suitable pour point reducers are condensation products of chlorinated paraffins with chlorinated naphthalene or with phenol and copolymers of ethene and vinyl acetate. Preference is given to polymers with unbranched aliphatic hydrocarbon side chains with at least 16 carbon atoms, such as polymers of alkyl esters of unsaturated monocarboxylic acids, in particular of acrylic acid and methacrylic acid, in which the alkyl chains are unbranched and

contain 16—22 carbon atoms and copolymers of these alkyl esters with other monomers such as vinylpyridines. The amount of pour point reducer that may be added to the LVI and MVI lubricating oils prepared according to the invention may vary within wide limits dependent on the pour-point-reducing effect of the additive concerned and the pour point reduction that is aimed at. In general the amount of pour point reducer applied is 0.01 to 1 % w.

In addition to the pour point reducers mentioned hereinbefore, also other quality-improving additives may be incorporated into the lubricating oils prepared according to the invention. Examples of such additives are antioxidants (e.g. alkyl phenols), detergent additives (e.g. calcium petroleum sulphonates, calcium alkylsalicylates and polyamines containing a hydrocarbon chain of at least 50 carbon atoms such as polyisobutenyltetraethylenepentamine) and high pressure additives such as zinc dialkyl dithiophosphates. Lubricating oils prepared according to the invention have a good colour and colour stability. These properties can be further improved by subjecting the lubricating oils to an activated earth treatment.

The lubricating oils prepared according to the invention may be used for various applications, for instance as lubricating oils for automotive engines, gear oils, axle oils, mould oils in concrete and foundry technology, in lubricating greases and printing inks and in the processing of rubbers and fibres.

The invention will now be illustrated with the aid of the following example.

EXAMPLE

Eight catalysts (catalysts A, B, and 1—6) were tested for the preparation of lubricating oils having a viscosity index lower than 90 using three aromatic extracts as the starting material (feeds I—III).

Catalysts A and B were prepared by impregnation of alumina carriers with aqueous solutions comprising a nickel, a molybdenum and a phosphorus compound followed by drying and calcining of the compositions. Catalyst A comprised 2.7 % w nickel, 11.6 % w molybdenum and 2.9 % w phosphorus. Catalyst B comprised 2.8 % w nickel, 12.2 % w molybdenum and 2.2 % w phosphorus. The preparation of catalysts 1—6 was carried out as follows.

Catalysts 1—4

Per 100 parts by weight of alumina, these catalysts all comprised 37 parts by weight of nickel, 70 parts by weight of tungsten and 14 parts by weight of fluorine. They were prepared via the hydrogel route starting from an alumina hydrogel from which by drying and calcining a xerogel could be obtained with a compacted bulk density of 0.35 g/ml and a

pore volume quotient of 0.8 (alumina hydrogel I).

The preparation of catalyst 1 was effected by mixing an aqueous solution containing a nickel and a tungsten compound with alumina hydrogel I, and maintaining the mixture for some time at an elevated temperature, separating the metal-loaded hydrogel from the mixture and then drying, extruding and calcining it. Fluorine was incorporated into catalyst 1 by in-situ fluoriding. The compacted bulk density of catalyst 1 was 1.5 g/ml.

The preparation of catalysts 2—4 was effected by mixing an aqueous solution containing a nickel, a tungsten and a fluorine compound with alumina hydrogel I, and maintaining the mixture for some time at elevated temperature, separating the metal and fluorine-loaded hydrogel from the mixture and then drying, extruding and calcining it. In the preparation of catalysts 3 and 4 75 and 25%, respectively, of the quantity of fluorine present on the ready catalyst was incorporated into the hydrogel. The additional quantity of fluorine (25% for catalyst 3 and 75% for catalyst 4) was incorporated into catalysts 3 and 4 by in-situ fluoriding. The compacted bulk densities of catalysts 2, 3 and 4 were 1.2, 1.2 and 1.3, respectively.

Catalysts 5 and 6

Per 100 parts by weight, these catalysts both comprised 5 parts by weight of nickel, 30 parts by weight of tungsten and 6 parts by weight of fluorine. They were prepared via the xerogel route. For the preparation of catalyst 5 the starting material was an alumina hydrogel from which by drying and calcining a xerogel could be obtained with a compacted bulk density of 0.70 g/ml and a pore volume quotient of 0.25 (alumina hydrogel II). For the preparation of catalyst 6 the starting material was an alumina hydrogel from which by drying and calcining a xerogel could be obtained with a compacted bulk density of 0.55 g/ml and a pore volume quotient of 0.40 (alumina hydrogel III). The preparation of catalysts 5 and 6 was effected by mixing an aqueous solution containing a fluorine compound with either alumina hydrogel II (for the preparation of catalyst 5), or alumina hydrogel III (for the preparation of catalyst 6), maintaining the mixture for some time at an elevated temperature, separating the fluorine-loaded hydrogel from the mixture and drying, extruding and calcining it, impregnating the extrudates with an aqueous solution comprising a nickel and a tungsten compound, and drying and calcining the impregnated extrudates. In the preparation of catalysts 5 and 6 60% of the quantity of fluorine present on the ready catalyst was incorporated into the hydrogel. The pore volume quotients of the xerogels that could be prepared from these fluorine-containing hydrogels by drying

and calcining were 0.6 and 0.7, respectively. The additional quantity of fluorine (40%) was incorporated into the catalysts 5 and 6 by in-situ fluoriding. The compacted bulk densities of catalysts 5 and 6 were 1.1 and 0.9 g/ml, respectively.

The feeds used had the following properties.

Feed I:

A furfural extract from a spindle oil fraction obtained by vacuum distillation of a paraffinic crude oil. The extract had an initial boiling point of 370°C, a D8 colour and produced 7.1 % w of sludge in the standard oxidation test.

Feed II:

A furfural extract from a medium machine oil fraction obtained by vacuum distillation of a paraffinic crude oil. The extract had an initial boiling point of 470°C, a D8 colour and produced 6.5 % w of sludge in the standard oxidation test.

Feed III:

A furfural extract from a residual lubri-

cating oil fraction deasphalted with propane, which fraction had been obtained by vacuum distillation of a paraffinic crude oil. The extract had an initial boiling point of 520°C, a D8 colour and produced 1.1 % w of sludge in the standard oxidation test.

The preparation of lubricating oils having a viscosity index lower than 90 using feeds I, II and III as the starting materials was effected by contacting these feeds at elevated temperature and pressure and in the presence of hydrogen with a fixed bed of one of catalysts A, B and 1-6. From the reaction products obtained end products were isolated by atmospheric distillation, which end products had initial boiling points which for the end products prepared from the distillate feeds were 100°C below that of the feed and which for the end products prepared from the residual feed were 200°C below that of the feed.

The conditions under which the catalytic hydrotreatments were carried out as well as some properties of the end products obtained are given in the following table.

TABLE

Exp. No.	Cat. No.	Feed No.	temp., °C	hydrogen partial pressure bar	space velocity, kg.l ⁻¹ .h ⁻¹	End product having an initial boiling point which for those prepared from a distillate was 100°C and for those prepared from a residual feed was 200°C below that of the feed		
						yield, % w	colour	sludge, % w
1	A	I	375	150	0.7	92	L 1.5	3.2
2	A	II	375	150	0.7	83	L 1.5	1.8
3	A	III	375	150	1.0	94	3.5	0.4
4	B	I	385	150	1.0	89	L 2	3.1
5	B	II	385	150	0.7	81	3	1.2
6	B	III	385	150	0.7	88	3.5	0.2
7	2	I	375	90	1.0	98	2	6.0
8	2	II	345	150	0.7	93	3	3.8
9	2	III	375	150	2.0	98	6	0.7
10	5	I	375	90	1.0	98	2	7.1
11	5	II	345	150	0.7	93	3	4.1
12	5	III	375	150	2.0	98	6	0.7
13	1	I	385	165	1.0	93	1.5	1.9
14	1	II	385	165	0.7	86	2	1.2
15	1	III	385	165	0.7	92	2.5	0.2
16	2	I	375	150	0.7	96	L 1.5	1.4
17	2	II	385	150	0.7	86	2.5	1.0
18	2	III	375	150	0.7	96	L 3	0.2
19	3	I	375	150	0.7	86	1.5	1.5
20	3	II	385	150	0.7	86	2.5	1.2
21	3	III	385	150	0.7	92	3	0.1
22	4	I	375	150	0.7	96	1.5	1.5
23	4	II	385	150	0.7	86	2.5	1.3
24	4	III	385	150	0.7	92	3	0.15
25	5	I	375	150	0.7	96	L 2	1.6
26	5	II	385	150	0.7	86	L 3	1.3
27	5	III	375	150	0.7	96	L 3	0.25
28	6	I	385	165	1.0	92	L 1.5	1.8
29	6	II	385	165	1.0	92	2.5	1.3
30	6	III	385	165	0.7	86	L 3	0.2

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All lubricating oils listed in the table under end products had a VI below 90.

Of the 30 experiments listed in the table only experiments 13—30 were carried out according to the invention. These experiments were all carried out at a temperature above 350°C, a hydrogen partial pressure above 100 bar and a space velocity below 1.5 kg.l⁻¹.h⁻¹ and with use of a hydrogel or xerogel catalyst according to the invention. In experiments 13, 14, 16, 17, 19, 20, 22, 23, 25, 26, 28 and 29 the requirements were met that starting from an aromatic extract from a distillate lubricating oil fraction, which extract is darker than 8 colour and produces more than 6 % w of sludge in the standard oxidation test, more than 85 % w of an oil is obtained having an initial boiling point 100°C below the initial boiling point of the feed, which oil is 3 colour or lighter and produces less than 3 % w of sludge in the standard oxidation test. In experiments 15, 18, 21, 24, 27 and 30 the requirements were met that starting from an aromatic extract from a de-asphalted residual lubricating oil fraction, which extract is darker than 8 colour and produces more than 0.5 % w of sludge in the standard oxidation test, more than 85 % w of an oil is obtained having an initial boiling point 200°C below the initial boiling point of the feed, which oil is 3 colour or lighter and produces less than 0.3 % w of sludge in the standard oxidation test.

Experiments 1—12 fall outside the scope of the present invention. They have been included in the patent application for comparison. In experiments 1—6 catalysts were used which did not belong to the group of hydrogel and xerogel catalysts according to the invention. This resulted in a low yield of product in experiments 2 and 5, a product producing too much sludge in the standard oxidation test in experiments 1, 3 and 4 and a product with an unsatisfactory colour in experiments 3 and 6. In experiments 7—12 the reaction conditions used were not correct. In experiments 7 and 10 the pressure was too low, in experiments 8 and 11 the temperature was too low and in experiments 9 and 12 the space velocity was too high. In all experiments this resulted in products producing too much sludge in the standard oxidation test and, in experiments 9 and 12, in products which moreover had an unsatisfactory colour.

WHAT WE CLAIM IS:—

1. A process for the preparation of lubricating oils having a viscosity index lower than 90, characterized in that the preparation is carried out by catalytic hydrotreatment of an aromatic extract from a distillate or de-asphalted residual lubricating oil fraction at a temperature above 350°C, a hydrogen partial pressure above 100 bar and a space velocity below 1.5 kg.l⁻¹.h⁻¹ and with use of fluorine-

containing catalysts comprising either nickel and/or cobalt and, in addition, molybdenum or nickel and tungsten on alumina as the carrier, which catalysts have a compacted bulk density of at least 0.8 g/ml, comprise at least 3 parts by weight of nickel and/or cobalt, at least 10 parts by weight of molybdenum and/or tungsten, respectively, per 100 parts by weight of carrier, and have been prepared from an alumina hydrogel from which, by drying and calcining, a xerogel can be obtained having a compacted bulk density of less than 0.8 g/ml.

1) If the pore volume quotient of the said xerogel is at least 0.5, the preparation of the catalyst is effected either

- a) by drying and calcining of the alumina hydrogel, incorporation of nickel and tungsten into the xerogel and once more drying and calcining the composition, or
- b) by incorporation of the metals into the alumina hydrogel, and drying and calcining the composition.

2) If the pore volume quotient of the said xerogel is less than 0.5, the preparation of the catalyst is effected, either

- a) by incorporation of at least part of the fluorine into the alumina hydrogel, and drying and calcining the composition, incorporation of nickel and tungsten into the xerogel and once more drying and calcining the composition, or
- b) by incorporation of the metals and at least part of the fluorine into the alumina hydrogel, and drying and calcining the composition, with the proviso in both (a) and (b) that sufficient fluorine should be incorporated into the alumina hydrogel to produce from this fluorine-containing alumina hydrogel, by drying and calcining, a xerogel having a pore volume quotient of at least 0.5.

2. A process according to claim 1, characterized in that a catalyst is employed which has been prepared by the xerogel route and comprises 3—12 parts by weight of nickel and 20—75 parts by weight of tungsten per 100 parts by weight of alumina.

3. A process according to claim 2, characterized in that a catalyst is employed in which the nickel-to-tungsten weight ratio is between 1:5 and 1:7.

4. A process according to any one of claims 1—3, characterized in that a catalyst is employed which has been prepared by the xerogel route and comprises 0.5—10 parts by weight of fluorine per 100 parts by weight of alumina.

5. A process according to claim 1, characterized in that a catalyst is employed which has been prepared by the hydrogel route and comprises 25—80 parts by weight of nickel

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All lubricating oils listed in the table under end products have a VI below 90.

5 Of the 30 experiments listed in the table only experiments 13—30 were carried out according to the invention. These experiments were all carried out at a temperature above 350°C, a hydrogen partial pressure above 100 bar and a space velocity below 1.5 kg.l⁻¹.h⁻¹ and with use of a hydrogel or xerogel catalyst according to the invention. In experiments 13, 14, 16, 17, 19, 20, 22, 23, 25, 26, 10 28 and 29 the requirements were met that starting from an aromatic extract from a distillate lubricating oil fraction, which extract is darker than 8 colour and produces more than 6 % w of sludge in the standard oxidation test, more than 85 % w of an oil is obtained having an initial boiling point 100°C below the initial boiling point of the feed, which oil is 3 colour or lighter and produces less than 3 % w of sludge in the standard oxidation test. In experiments 15, 18, 21, 24, 20 27 and 30 the requirements were met that starting from an aromatic extract from a de-asphalted residual lubricating oil fraction, which extract is darker than 8 colour and produces more than 0.5 % w of sludge in the standard oxidation test, more than 85 % w of an oil is obtained having an initial boiling point 200°C below the initial boiling point of the feed, which oil is 3 colour or lighter and produces less than 0.3 % w of sludge in the standard oxidation test.

35 Experiments 1—12 fall outside the scope of the present invention. They have been included in the patent application for comparison. In experiments 1—6 catalysts were used which did not belong to the group of hydrogel and xerogel catalysts according to the invention. This resulted in a low yield of product in experiments 2 and 5, a product producing too much sludge in the standard oxidation test in experiments 1, 3 and 4 and a product with an unsatisfactory colour in experiments 40 3 and 6. In experiments 7—12 the reaction conditions used were not correct. In experiments 7 and 10 the pressure was too low, in experiments 8 and 11 the temperature was too low and in experiments 9 and 12 the space velocity was too high. In all experiments this resulted in products producing too much sludge in the standard oxidation test and, in experiments 9 and 12, in products which moreover had an unsatisfactory colour.

55 **WHAT WE CLAIM IS:—**

1. A process for the preparation of lubricating oils having a viscosity index lower than 90, characterized in that the preparation is carried out by catalytic hydrotreatment of 60 an aromatic extract from a distillate or de-asphalted residual lubricating oil fraction at a temperature above 350°C, a hydrogen partial pressure above 100 bar and a space velocity below 1.5 kg.l⁻¹.h⁻¹ and with use of fluorine-

containing catalysts comprising either nickel and/or cobalt and, in addition, molybdenum or nickel and tungsten on alumina as the carrier, which catalysts have a compacted bulk density of at least 0.8 g/ml, comprise at least 3 parts by weight of nickel and/or cobalt, at least 10 parts by weight of molybdenum and/or at least 20 parts by weight of tungsten, respectively, per 100 parts by weight of carrier, and have been prepared from an alumina hydrogel from which, by drying and calcining, a xerogel can be obtained having a compacted bulk density of less than 0.8 g/ml:

- 1) If the pore volume quotient of the said xerogel is at least 0.5, the preparation of the catalyst is effected either
 - a) by drying and calcining of the alumina hydrogel, incorporation of nickel and tungsten into the xerogel and once more drying and calcining the composition, or
 - b) by incorporation of the metals into the alumina hydrogel, and drying and calcining the composition.
- 2) If the pore volume quotient of the said xerogel is less than 0.5, the preparation of the catalyst is effected, either
 - a) by incorporation of at least part of the fluorine into the alumina hydrogel, and drying and calcining the composition, incorporation of nickel and tungsten into the xerogel and once more drying and calcining the composition, or
 - b) by incorporation of the metals and at least part of the fluorine into the alumina hydrogel, and drying and calcining the composition, with the proviso in both (a) and (b) that sufficient fluorine should be incorporated into the alumina hydrogel to produce from this fluorine-containing alumina hydrogel, by drying and calcining, a xerogel having a pore volume quotient of at least 0.5.
2. A process according to claim 1, characterized in that a catalyst is employed which has been prepared by the xerogel route and comprises 3—12 parts by weight of nickel and 20—75 parts by weight of tungsten per 100 parts by weight of alumina.
3. A process according to claim 2, characterized in that a catalyst is employed in which the nickel-to-tungsten weight ratio is between 1:5 and 1:7.
4. A process according to any one of claims 1—3, characterized in that a catalyst is employed which has been prepared by the xerogel route and comprises 0.5—10 parts by weight of fluorine per 100 parts by weight of alumina.
5. A process according to claim 1, characterized in that a catalyst is employed which has been prepared by the hydrogel route and comprises 25—80 parts by weight of nickel



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and 50—80 parts by weight of tungsten per 100 parts by weight of alumina.

6. A process according to claim 5, characterized in that a catalyst is employed in which the nickel-to-tungsten weight ratio is between 1:1.5 and 1:5.

7. A process according to claim 1, characterized in that a catalyst is employed comprising 25—80 parts by weight of nickel and/or cobalt and 50—80 parts by weight of molybdenum per 100 parts by weight of alumina.

8. A process according to claim 7 characterized in that a catalyst is employed in which the weight ratio between nickel and/or cobalt on the one hand and molybdenum on the other is between 1:1 and 1:5.

9. A process according to any one of claims 1 and 5—8, characterized in that a catalyst is employed which has been prepared by the hydrogel route and comprises 10—25 parts by weight of fluorine per 100 parts by weight of alumina.

10. A process according to any one of claims 1—9, characterized in that an aromatic extract from a lubricating oil fraction originating from a paraffinic crude oil is used as the starting material.

11. A process according to any one of claims 1—10, characterized in that the catalytic hydrotreatment is carried out at a temperature below 425°C and preferably below 400°C, a hydrogen partial pressure below 200 bar and preferably below 175 bar, a space velocity above 0.5 kg.l⁻¹.h⁻¹ and a hydrogen/oil ratio of from 250 to 2500 NI.kg⁻¹ and preferably of from 500 to 2000 NI.kg⁻¹.

12. A process according to any one of claims 1—11, characterized in that the lubricating oil obtained is further subjected to an activated earth treatment.

13. A process for the preparation of lubricating oils with a viscosity index lower than 90, substantially as described hereinbefore and in particular with reference to experiments 13—30 from the example.

14. Lubricating oils with a viscosity index lower than 90, prepared according to a process as described in claim 13.

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