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(54) PROCESS FOR THE PREPARATION OF LUBRICATING OIL

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPIJ B.V. formerly Shell Internationale Research Maatschappij N.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 oil with a high viscosity index.

The Applicants have found that lubricating oil with a high viscosity index can be prepared from high boiling mineral oil fractions by converting the latter by means of hydrogen in the presence of a phosphorous containing catalyst.

According to the present invention a process for the preparation of lubricating oil with a high viscosity index is characterised in that a high boiling mineral oil fraction is contacted at elevated temperature and pressure, in the presence of hydrogen, with a catalyst consisting of nickel and/or cobalt and molybdenum and/or tungsten in metallic, oxidic and/or sulphidic form, and of phosphorous oxide supported on a catalyst carrier consisting of refractory oxide.

Suitable starting materials for the process according to the invention are high boiling hydrocarbon mixtures, e.g. heavy petroleum fractions and heavy fractions obtained by pyrolysis of coal, bituminous shale or tar sand. Petroleum fractions boiling at least in part above the boiling range of lubricating oil may be used to advantage. As feed for the present process use is preferably made of a distillate fraction recovered by vacuum distillation from

a residual oil fraction obtained by atmospheric distillation. The boiling range of such a vacuum distillate is usually between 350°C and 550°C. However, de-ashed residual petroleum fractions are particularly preferred.

The process according to the invention is carried out at elevated temperature and pressure and in the presence of hydrogen or a hydrogen containing gas. Pure hydrogen may be used, but this is not necessary. A gas with a hydrogen content of 70% or more by volume is perfectly suitable. In practice it will be preferable to use a hydrogen containing gas originating from a catalytic reforming plant. Such a gas not only has a high hydrogen content but also contains low-boiling hydrocarbons, for example, methane, and a small quantity of propane.

The temperature and pressure used in the present process may vary between very wide limits, depending on the desired degree of conversion. Suitably, the temperature selected will not be below 350°C and not above 550°C. At temperatures below 350°C the rate of conversion is reduced, whereas at temperatures above 550°C cracking occurs to such an extent that only a limited quantity of the desired product is obtained. A temperature between 400°C and 500°C is preferred. Pressures lower than 50 bar are less desirable since they reduce the life of the catalyst while involving the risk of too high an aromatics content in the product, as a result of which the viscosity index is adversely affected. A pressure above 250 bar would require a very costly installation. It is preferable to use a pressure between 100 and 200 bar.

The liquid hourly space velocity and the hydrogen/oil ratio are likewise selected between very wide limits. It is preferred,

however, to select a liquid hourly space velocity between 0.1 and 10 kg of oil per hour per litre of catalyst. A liquid hourly space velocity of less
5 0.1 kg/hour per litre of catalyst would require an uneconomically large reactor for a given degree of conversion, whereas a liquid hourly space velocity of more than 10 kg per hour
10 per litre of catalyst would give only a low degree of conversion into the desired product. The hydrogen/oil ratio is preferably between 100 and 5000 standard litres (litres at 1 bar and at 0°C) per kg of oil. A very low H_2 /oil ratio would adversely affect the life of the
15 catalyst, whereas a very high H_2 /oil ratio would cause a considerable loss of pressure over the catalyst beds, so that much energy for compression would be required for circulating the hydrogen-rich gas.

20 The catalyst used in the process according to the invention contains at least two hydrogenative metal components, a carrier and phosphorus.

25 One of the metal components consists of nickel and/or cobalt, and/or nickel and/or cobalt compound; moreover the catalyst should contain molybdenum and/or tungsten and/or molybdenum and/or tungsten compound. Important factors in this respect
30 are the quantity of hydrogenative metal component expressed as a percentage of the total catalyst, as well as the ratio between nickel and/or cobalt on the one hand and molybdenum and/or tungsten on the other.

35 The metal component should preferably not be used in too small quantities since this would have an adverse effect on the desired hydrogenating action. A very high load of metal component would cause the pores of the
40 porous catalyst support to become clogged in such a manner that part of the surface of the catalyst would be rendered inaccessible to the material to be converted. It has now been found that a catalyst containing between 3%
45 and 16% by weight of nickel and/or cobalt (hereinafter mentioned as the metals A) and between 6% and 24% by weight of molybdenum and/or tungsten (hereinafter indicated as the metals B) is pre-eminently suitable for
50 the process according to the invention. For this reason it is preferred to apply the above-mentioned percentages by weight of hydrogenative metal components to the catalyst before using the latter for the present process.

55 In a comparative investigation of catalysts which according to the present invention are suited to be applied in the preparation of lubricating oil with high viscosity index it has been found that catalysts in which the atomic
60 ratio of the metals A to the metals B is below 0.75:1 show a lower temperature requirement and retention of aromatics and a higher selectivity than catalysts with the same content of metals B but in which the atomic ratio of
65 the metals A to the metals B is above 0.75:1.

An improved embodiment of the present invention therefore consists in that a catalyst is applied in which the atomic ratio of the
70 metals A to the metals B is below 0.75:1.

When using such catalysts the preparation
75 of lubricating oil according to the invention is preferably carried out at a temperature of 375—425°C, a pressure of 100—200 kg/cm², a space velocity of 0.5—1.5 kg of feed per litre of catalyst per hour and a hydrogen/feed
80 ratio of 500—2500 NI of hydrogen per kg of feed.

There is a special preference for catalysts containing the metals nickel and molybdenum or the metals nickel and tungsten. With regard
85 to the atomic ratio of the metals A to the metals B, catalysts, in which this atomic ratio is between 0.2:1 and 0.65:1, are preferred.

The amount of phosphorus applied to the catalyst may likewise vary between wide
90 limits. It has been found, however, that the activity of the catalyst depends on the percentage by weight of phosphorus present in the catalyst. Good activity of the catalyst is ensured by a phosphorous content of between
95 1% and 12% by weight, calculated as P_2O_5 . For this reason it is preferred to use a catalyst having such a phosphorus content. More preferably the phosphorus content is selected between 2% and 9% by weight calculated as
100 P_2O_5 on the total catalyst and it has been found that the maximum activity of the catalyst is obtained at a phosphorus content between 3% and 7% by weight, likewise calculated as P_2O_5 on the total catalyst.

“Activity” in this specification means the
105 temperature required for obtaining under given operating conditions (pressure, liquid hourly space velocity, H_2 /oil ratio) and starting from a given feed, a product with a pre-determined viscosity index. The higher the activity of the catalyst used the lower will be the temperature required.

Although nickel, in combination with
110 molybdenum and/or tungsten, as well as cobalt in combination with either or both of the latter metals, are suitable for use as one of the two hydrogenating components of the catalyst for effecting the conversion according
115 to the invention, the best results are obtained by a combination of nickel and molybdenum. For this reason the use of a combination of these metals is preferred.

In principle any refractory material may be employed as carrier for the catalyst to be used.
120 Suitable materials are for example alumina (aluminium oxide), silica, magnesia (magnesium oxide), titanium oxide, zirconia (zirconium oxide), thoria (thorium oxide), boria (boron oxide) and mixtures and compounds of
125 these metal oxides.

It has now been found that the use of
130 alumina or a mixture of silica and magnesia as carrier material permits the preparation of catalysts with a particularly good activity,

selectivity and stability. For this reason use is preferably made of these carrier materials.

Commercial alumina usually contains small quantities of impurities, especially silica and sodium. It has been found that alumina containing between 0.5% and 3% by weight of silica and up to 0.005% by weight of sodium is an excellent carrier material for the catalyst. This alumina is therefore preferred.

If the alumina contains more than 0.005% by weight of sodium, the sodium content may be reduced to the required level by ion exchange with a solution of an ammonia salt.

Of the supports composed of silica and magnesia, a mixture of between 50% and 90% by weight of silica and between 10% and 50% by weight of magnesia is preferred.

In this specification the selectivity of a catalyst is understood to mean the yield of lubricating oil with a specified viscosity index which has been obtained under given conditions (temperature, pressure, liquid hourly space velocity and H_2 /oil ratio) with the aid of the catalyst in question. The stability of a catalyst is the extent to which the catalyst retains its activity during prolonged use in the process according to the invention.

To further increase the activity and selectivity of the catalyst fluorine is added thereto. It has been found that an improvement is even obtained by adding only 1% by weight of fluorine. If more than 6% by weight is added there is a risk, however, that the selectivity of the catalyst may be adversely affected. For this reason it is preferred to add between 1% and 6% by weight of fluorine to the catalyst.

The catalyst may be prepared in any manner desired, for example, by impregnating the carrier with one or more aqueous solutions of compounds of the other components, followed by drying and calcination. If the impregnation is carried out in more steps the material may be dried and calcined, if desired between the successive steps of impregnation.

Examples of suitable water-soluble compounds of nickel, cobalt, molybdenum, tungsten and phosphorus, which can be applied in the preparation of the present catalysts, are nitrates, chlorides, carbonates and formates of nickel and cobalt, ammonium molybdate, ammonium tungstate, phosphoric acid, ammonium phosphate and ammonium hydrophosphate. In order to obtain a higher solubility of these compounds and for the stabilization of the solutions certain compounds, such as ammonium hydroxide, monoethanolamide and sorbitol may be added to the solutions.

As already indicated above, a preferred catalyst contains a carrier, nickel, molybdenum and phosphorus. Such a catalyst can be prepared very conveniently by impregnating a catalyst carrier with an aqueous phosphoric acid solution, drying the impregnated carrier

and subsequently impregnating it with an aqueous solution of a molybdate and a nickel salt, whereupon the catalyst is finished by drying and calcining.

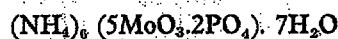
It has been found, however, that catalysts of even better activity, stability and selectivity can be prepared by impregnation with an aqueous solution containing both a phosphomolybdate and a nickel salt rather than with two separate solutions one containing phosphoric acid and the other comprising a molybdate and nickel salt.

Accordingly, the catalysts which are used to advantage in the process according to the invention, are prepared as follows:

A catalyst carrier is impregnated with an aqueous solution of an acid or non-acid phosphomolybdate and a nickel salt, whereupon the impregnated carrier is dried and calcined.

As a nickel salt, use is preferably made of nickel hexamine dichloride $[(Ni(NH_3)_6]Cl_2]$, or nickel formate, although any water-soluble nickel salt, such as nickel nitrate and nickel chloride may be employed.

As phosphomolybdate and acid phosphomolybdate use is preferably made of ammonium 2-phospho-5-molybdate and acid ammonium 2-phospho-5-molybdate respectively. These substances have respectively the following chemical formulae:



and



They are described in "Nouveau Traité de Chimie Minérale" (1959), edited by Paul Pascal, Volume XIV, pages 913, 916 and 917 and in "Polyanions et Polycations" (1963) by M. P. Souchay, page 160.

Although it is preferred in the above-described methods for the preparation of catalysts to apply the nickel salt to the catalyst by impregnation together with the phosphomolybdate and/or the acid phosphomolybdate, good results may also be obtained by treating the catalyst with two separate solutions, one containing the nickel salt and the other containing the phosphomolybdate and/or acid phosphomolybdate.

In order to ensure that the nickel salt, the phosphomolybdate and/or the acid phosphomolybdate are thoroughly dispersed on the catalyst during impregnation, it is preferred to add ammonium hydroxide to the solutions of these components, the quantity to be added being such that the pH of these solutions is between 7 and 12.

The specification of our co-pending U.K. Patent Application 31415/73, which has been divided out of this application, claims the preparation of a catalyst by impregnating an oxidic catalyst carrier with a solution of

ammonium-2-phospho-5-molybdate and/or acid ammonium-2-phospho-5-molybdate and a nickel salt, and by drying and calcining of the impregnated carrier.

- 5 Although an active catalyst may even be obtained by means of only one impregnation with the appropriate solution of nickel salt and ammonium - 2 - phospho - 5 - molybdate and/or acid ammonium - 2 - phospho - 5 - molybdate, it is preferred, in order to obtain even more active catalysts with a higher content of nickel, phosphorus and molybdenum to repeat the impregnation several times, the impregnated carrier being dried between two successive impregnation steps. To obtain an excellent catalyst three impregnations will be a rule be sufficient while if, depending on the concentration of the impregnating solution, impregnation is repeated more than 10 times, this may involve the risk of too large an amount of nickel, phosphorus and/or molybdenum being applied to the catalyst, resulting in the clogging of the pores of the carrier. For this reason the number of impregnating steps is preferably between 3 and 10.

- 15 In between the successive impregnations and after the final impregnation the catalyst is dried. This is preferably effected for between 0.5 and 5 hours at a temperature between 100°C and 250°C.

- 20 As noted previously, the catalyst preferably contains fluorine. This element may be applied to the catalyst by any suitable method. For this purpose it is preferred to impregnate the catalyst with a solution of hydrogen fluoride, ammonium fluoride and/or ammonium bifluoride. These components have the advantage that they do not leave behind less desirable cations such as Na, K and Ca ions on the catalyst after calcination.

- 25 The catalyst is completed by calcination. This treatment is preferably carried out at a temperature between 450°C and 850°C, for between 0.5 and 5 hours.

- 30 After calcination, the phosphorus and the metals, viz, nickel and/or cobalt and molybdenum and/or tungsten, are probably present in the catalyst in the form of oxides, although the possibility cannot be excluded that they have combined, at least in part, with the catalyst carrier.

- 35 It has been found that, in the catalytic conversion of heavy hydrocarbon mixtures to lubricating oil by means of hydrogen, better results can be obtained if the catalyst is previously sulphided, by which process the metal oxides are converted, at least in part, to the corresponding metal sulphides.

- 40 For this reason it is preferred to use a sulphided catalyst.

- 45 Sulphiding of the present catalysts may be carried out according to the well-known sulphiding methods for catalysts. Sulphiding may be effected, for instance, by treating the catalysts with a sulphur-containing gas such as a

mixture of hydrogen and hydrogen sulphide, a mixture of hydrogen and carbon disulphide or a mixture of hydrogen and a mercaptan, such as butyl mercaptan.

A very good and hence preferred sulphiding method consists in contacting the catalyst at a temperature of between 250°C and 450°C, a pressure of between 30 and 70 bars, an hourly space velocity of between 1 and 10 kg of oil per hour per litre of catalyst and a hydrogen/oil ratio of between 50 and 500 standard litres of H₂ per kg of oil with an oil which contains sulphur compounds, preferably with a gas oil which contains sulphur compounds. This treatment is preferably given in the same reaction vessel in which the hydrogenative conversion to lubricating oil is carried out.

Once the catalyst has been sulphided, the starting material for the production of lubricating oil with a high viscosity index is introduced into the reactor at a suitable temperature, pressure, hourly space velocity and H₂/oil ratio and passed over the catalyst which is preferably present in one or more beds of particles with a size between 0.5 and 3 mm.

After passing through the reactor the reaction product is cooled and separated into a hydrogen-rich gas and a liquid product.

The hydrogen-rich gas is preferably recycled, at least in part to the reactor. The liquid product contains hydrocarbons boiling below the boiling range of lubricating oil and hydrocarbons boiling with the boiling range of lubricating oil.

The hydrocarbons boiling below the boiling range of lubricating oil are preferably separated from the higher boiling residue by fractional distillation. The cut point of this distillation is preferably so chosen that the higher boiling residue has an initial boiling point in the range between 350°C and 400°C.

In addition to excellent lubricating components this residue normally contains paraffins which solidify at a slightly reduced temperature and thus have an adverse effect on the pour point of the desired lubricating oil. In order to prepare a useful lubricating oil of lubricating oil component from the residue, it is therefore preferred to dewax this residue, thus separating slack wax therefrom. This treatment can be carried out in any manner desired. The dewaxing is preferably carried out by means of a mixture of methylethylketone and toluene at a temperature between -10°C and -40°C and a volume ratio of solvent to oil between 1:1 and 10:1.

The dewaxed residue has a high viscosity index, for example, a viscosity index between 100 and 140, depending on the conditions under which the hydrogenative conversion of the starting material took place.

For this reason it is eminently suitable for use as multigrade lubricating oil or multi-

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grade lubricating oil component. Moreover this dewaxed residue permits the preparation by means of vacuum distillation of one or more lubricating oils or lubricating oil components with high viscosity indices and mutually different viscosities, which oils or components in their turn may be worked up into excellent multigrade lubricating oils by blending them together or with other components.

According to a preferred embodiment of the invention the slack wax obtained in the dewaxing treatment is catalytically isomerized in the presence of a hydrogen-containing gas. This hydromerization is preferably carried out under the following conditions:

Temperature: 310—450°C

Pressure: 50—200 bars absolute

Space velocity: 0.1—5.0 litres of slack wax per hour per litre of catalyst

Hydrogen/slack wax ratio: 100—5000 litres of H_2 (N.T.P.) per kg of slack wax.

The catalyst used in the hydroisomerization zone contains a component having hydroisomerization activity, which has been combined with an acid refractory solid support having isomerization activity.

The quantity of hydrogenation component may vary within wide limits, advantageously of from 0.5 to 40% by weight, calculated on the total catalyst, the remainder being formed by the solid acid refractory support.

The hydrogenation component of the catalyst preferably contains one or more metals of Groups IB, IIB, VB, VIB, VIIB and/or VIII of the Periodic Table of Elements and/or one or more oxides and/or sulphides of one or more of these metals.

Groups IB, IIB, VB, VIB, VIIB and VIII of the Periodic Table of Elements comprise the following metals: Cu, Ag, Au, Zn, Cd, Hg, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt.

In the hydroisomerization zone a sulphur-resistant catalyst is preferably used, since even relatively small quantities of sulphur which may be present in the recycle gas to be used in the present process have a tendency to poison catalysts which are sulphur-sensitive, so that their activity and selectivity are unfavourably influenced. Especially active sulphur-resistant catalysts comprise one or more oxides and/or sulphides of Group VIB (Cr, Mo, V) and/or of the iron group (Fe, Ni, Co). A very much preferred catalyst to be used for the hydroisomerization contains 6 to 24% by weight tungsten and/or molybdenum and 3 to 18% by weight nickel and/or cobalt in the form of their oxides and/or sulphides.

The acid-acting refractory support of the catalyst to be used in the hydroisomerization zone advantageously comprises a mixture and/or a compound of silica and alumina, of alumina and BF_3 , of silica and magnesia, of

silica, alumina and zirconia, or of alumina and P_2O_5 . Acid-treated clays and zeolitic crystalline molecular sieves are also very useful for this purpose. To increase the activity of the catalyst fluorine is preferably added, advantageously in an amount of 1 to 6% by weight, to the support, thus increasing its acidity.

The most preferred catalyst for the hydroisomerization zone contains 3 to 18% by weight nickel, 6 to 24% by weight molybdenum, 1 to 6% by weight fluorine and 2 to 9% by weight P_2O_5 deposited on a support consisting entirely or principally of alumina.

If the product leaving the hydrocracking zone and the hydrogen-containing gas both have a very small sulphur content, a sulphur-sensitive catalyst can be used in the hydroisomerization zone. By using such a catalyst a higher yield of luboil can be obtained calculated on the basis of the slack wax feedstock. A suitable sulphur-sensitive catalyst contains platinum on an alumina support, the acidity of which has been increased by the incorporation of chlorine or fluorine, the latter being preferred.

With catalysts containing more than 1.0% by weight fluorine better results are obtained in the hydroisomerization zone than with catalysts containing less fluorine. In order to avoid excessive cracking and to maintain a good selectivity it is moreover preferable to use not more than 6.0% by weight fluorine in the hydroisomerization catalyst.

The hydroisomerization conversion is as a rule not complete when carried out in one pass. Therefore in many cases the non-converted slack wax should be removed from the oil obtained as a result of the hydroisomerization. This is done by dewaxing.

Small quantities boiling below the boiling range of luboil can be present in the effluent of the hydroisomerization zone, since in this zone some cracking occurs. It is preferable to exclude these low boiling components from the oil/slack wax mixture to be dewaxed, because they form an undesirable diluent and reduce the efficiency of the dewaxing operation. The feed to the second dewaxing zone is thus preferably formed by that part of the hydroisomerization effluent which boils within the luboil boiling range. The entire normally liquid part, including neopentane and higher boiling hydrocarbons, of the hydroisomerization effluent or any desired fraction thereof may, however, be used in the second dewaxing zone as long as hydrocarbons boiling in the luboil boiling range are included.

By the term "hydrocarbons boiling in the luboil boiling range" is meant high-boiling hydrocarbons having a viscosity which makes them suitable as luboil components. Although certain luboils may be more volatile, the majority of luboils have an initial boiling point of at least 350°C at atmospheric pressure.

The separation of hydrocarbons boiling

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below the luboil boiling range from the hydroisomerization effluent is suitably effected by fractional distillation or flash distillation. Other separation methods may, however, be used.

The dewaxing of the portion boiling in the luboil boiling range obtained from the hydroisomerization effluent may be carried out in any conventional way. Dewaxing with the aid of a solvent is suitably used. In this operation a waxy feed is dissolved in an organic solvent and the solution is then cooled to crystallize the wax, which is separated by filtration off the solvent/wax mixture. Suitable solvents for this operation are liquid propane, benzene, toluene, methylethylketone, and mixtures of methylethylketone and one or more aromatics.

The dewaxing of the portion boiling in the luboil boiling range of the hydroisomerization effluent is preferably carried out with a mixture of 40 to 60 parts by volume of methylethylketone and 60 to 40 parts by volume of toluene, at a temperature in the range of from -10°C to -40°C , the volumetric ratio of solvent to oil being in the range of from 1:1 to 10:1.

The slack wax obtained in the second dewaxing treatment is advantageously recycled to the hydroisomerization zone.

The dewaxed oil has a very high viscosity index, ranging from 140 to 170, depending on the hydroisomerization conditions. Therefore it can excellently be applied as a multigrade luboil or as multigrade luboil component.

The dewaxed residue may also be separated by vacuum distillation into a plurality of luboils or luboil components with very high viscosity indices and mutually different viscosities. These luboil components may be used for the production of excellent multigrade luboils by blending them with each other or with other luboil components.

In order to simplify the process the hydrocracking treatment and the hydroisomerization are advantageously carried out over the same catalyst, which comprises—as has already been mentioned hereinbefore—nickel and/or cobalt, molybdenum and/or tungsten, phosphorus and preferably fluorine deposited on a refractory oxidic support.

This catalyst may be present in two reactors, the hydrocracking being carried out in the first reactor and the hydroisomerization in the second.

It is also possible to carry out the hydrocracking and the hydroisomerization in the same reaction vessel. In this way only one reactor is needed and a considerable improvement in the economy of the process is achieved.

As has already been mentioned hereinbefore the non-converted slack-wax, which has been separated from the hydroisomerization product can be recycled to the hydroisomerization

reactor in order to be converted into luboil with a very high viscosity index.

In case the hydrocracking treatment and the hydroisomerization take place in the same reaction vessel, the slack wax separated from the hydroisomerization product is preferably passed together with the highboiling mineral oil fraction to this reaction vessel and to subject the blend of high boiling mineral oil fraction and slack wax to a combined hydroisomerization/hydrocracking treatment.

The invention will now be further elucidated by means of the following Examples.

EXAMPLE 1

A catalyst A for the hydrogenative conversion of heavy hydrocarbon oils to lubricating oil with a high viscosity index was prepared as follows:

250 g of particles obtained by extrusion, with a diameter of 1.3 mm and consisting of alumina, were impregnated for 20 hours at a temperature of 22°C with a solution of 15.5 ml of 85% phosphoric acid (H_3PO_4) in 241.5 ml of water.

The impregnated carrier was subsequently dried for 2 hours.

After this period, a solution of 93 g of ammonium paramolybdate in 270 ml of water was mixed with a solution of 118 g of nickel hexamine dichloride in a mixture of 160 ml of water and 11 ml of 27% ammonium hydroxide.

The dried catalyst carrier was impregnated three times for 10 minutes at a temperature of 22°C with the solution of ammonium paramolybdate, nickel hexamine dichloride and ammonium hydroxide described above, the carrier being dried between the impregnating steps, each time for 2 hours at 200°C . After the final impregnating step, the impregnated carrier was dried for 16 hours at 120°C and calcined for 2 hours at a temperature of 650°C .

The catalyst thus prepared had the following composition:

	% by weight
Alumina (Al_2O_3)	66
Phosphorus pentoxide (P_2O_5)	4
Molybdenum oxide (MoO_3)	20
Nickel oxide (NiO)	10

EXAMPLE 2

A catalyst B for the hydrogenative conversion of heavy hydrocarbon oils to lubricating oil with a high viscosity index was prepared in the following manner:

116 g of ammonium 2-phospho-5-molybdate were dissolved in 395 ml of water to which 100 ml of 27% ammonium hydroxide had been added.

117 g of nickel hexamine dichloride were dissolved in 800 ml of water to which 20 ml of 27% ammonium hydroxide had been added. The phosphomolybdate solution and

the nickel hexamine dichloride solution were subsequently mixed together.

250 g. of alumina extrudates, which were identical to the alumina extrudates used in Example 1, were subsequently impregnated for 10 minutes with the aqueous mixture containing the phosphomolybdate, the nickel hexamine dichloride and ammonium hydroxide. This impregnation was repeated six times, the impregnated carrier being dried between the steps, each time at 200°C for 2 hours.

After the final impregnation, the carrier was dried for 2 hours at 120°C and subsequently calcined for 2 hours at 650°C.

The catalyst thus produced had the following composition:

	% by weight
Alumina (Al_2O_3)	66
Phosphorus pentoxide (P_2O_5)	4
Molybdenum oxide (MoO_3)	20
Nickel oxide (NiO)	10

EXAMPLE 3

A catalyst C was prepared by impregnating a quantity of 150 g of catalyst B for 1 hour at 20°C with a mixture of 11 ml of 40% hydrogen fluoride and 90 ml of water. The fluorinated catalyst was subsequently dried for 12 hours at 120°C and calcined for 2 hours at 650°C.

Catalyst C had the following composition:

	% by weight
Alumina (Al_2O_3)	64.0
Phosphorus pentoxide (P_2O_5)	3.9
Molybdenum oxide (MoO_3)	19.4
Nickel oxide (NiO)	9.7
Fluorine (F)	3.0

EXAMPLE 4

A residual oil fraction obtained from a North African crude oil and deasphalted by means of a liquid propane was used to test the activity, the selectivity and the stability of catalysts A, B and C.

This oil fraction had the following properties:

Specific gravity 20/4: 0.907
Viscosity at 99°C: 32.8 cS
Viscosity index (VI_E) ASTM—D 2270 after dewaxing at -19°C: 77
Yield of dewaxed oil after dewaxing at -19°C: 89.2% by weight.

Quantities of this oil fraction were passed over three identical beds of the catalysts A, B and C under the following reaction conditions:

Pressure: 140 bars absolute
Hourly space velocity: 1 kg of oil per hour per litre of catalyst
Hydrogen/oil ratio: 1000 standard litres of H_2 per kg of oil.

During the catalytic conversions over the three catalyst beds the temperatures were controlled in such a manner that the products of the three treatments, after distillative removal of components boiling below 375°C and after dewaxing, had a viscosity index (VI_E) of 130.

The dewaxing was effected by means of a mixture of methylethylketone and toluene (50/50) in the ratio of three parts by volume of mixture to one part by volume of oil at a temperature of -19°C.

The following temperatures were required to obtain the above-mentioned results:

for catalyst A : 457°C
for catalyst B : 452°C
for catalyst C : 441°C.

At these temperatures the following yields of dewaxed oil with a VI_E of 130 and an initial boiling point of 350°C calculated on the original North African dewaxed residual oil fraction used as starting material were obtained:

for catalyst A : 25% by weight
for catalyst B : 29% by weight
for catalyst C : 32% by weight.

From the foregoing it is evident that phosphorus-containing catalyst display a very good activity and selectivity for the production of lubricating oil with a very high viscosity index and that these properties can be further improved by preparing the catalysts with the aid of ammonium-2-phospho-5-molybdate and adding fluorine thereto.

The three catalysts A, B and C also have an excellent stability. This was borne out by the fact that during the first 700 hours the temperature had to be increased by approximately 2°C per 100 hours to ensure maintenance of the desired viscosity index $\text{VI}_E=130$, whereas after 700 hours and up to the end of the experiments described above, i.e. after 1100 hours, the temperature could be kept constant to achieve the desired result ($\text{VI}_E=130$) at all times.

EXAMPLE 5

Preparation of Catalysts

Catalyst I

A solution of 37 g of ammonium heptamolybdate and 11 g of ammonium phosphate in 40 ml of water and a solution of 22 g of nickel formate 2 aq in 40 ml 25% NH_4OH were combined. After addition of water to obtain 90 ml, this solution was applied for a one-step impregnation of 100 g of 1.5 mm alumina extrudates (pore volume: 0.62 ml/g; specific surface area: 219 m^2/g ; silica content 1.4%w). The impregnated alumina was dried at 120°C for two hours and calcined at 500°C for three hours.

Catalyst A

A solution of 28.19 g of $(\text{NH}_4)_2\text{HPO}_4$ in 60 ml of water and a solution of 92.9 g of ammonium heptamolybdate in 335 ml of water were combined. To this solution 100 ml of 25% NH_4OH and a solution of 120.55 g of nickel chloride 6 aq in a mixture of 300 ml of water and 233 ml of 25% NH_4OH were successively added. The resulting solution (1028) ml was applied for a six-step impregnation of 250 g of the same alumina extrudates which were used for the preparation of catalyst I. The impregnation was effected by immersing the alumina extrudates into the afore-mentioned solution five times for ten minutes. After each immersion the alumina was filtered off and dried at 120°C for two hours. After the fifth immersion the remaining quantity of impregnating liquid amounted to 140 ml. With this liquid the alumina extrudates were impregnated for the sixth time. After the sixth impregnation the alumina was dried at 120°C for two hours and calcined at 500°C for three hours.

Catalyst B

This catalyst was prepared in completely the same way as catalyst A, but starting from a different carrier material (1.3 mm alumina extrudates with a pore volume of 0.67 ml/g and a specific surface area of 221 m^2/g).

Catalyst C

A solution of 64.8 g of aluminium heptamolybdate in 80 ml of water and a solution

of 19.4 g of $(\text{NH}_4)_2\text{HPO}_4$ in 80 ml of water were combined. To this solution a solution of 84.4 g of nickel chloride 6 aq in 70 ml of monoethanolamine was added. After the addition of water to obtain 320 ml, this solution was divided into two equal portions which were applied for the impregnation of 175 g of the same alumina extrudates that were used for the preparation of catalyst I. The impregnation was effected in two steps, each with a portion of the afore-mentioned solution. After each impregnation the alumina was dried at 120°C for two hours and calcined at 500°C for three hours.

Catalyst D

While heating an adding dropwise 30 g of 30% H_2O_2 , 64.8 g of ammonium heptamolybdate were dissolved in 60 ml of water. After cooling to room temperature the solution was combined with a solution of 103 g of nickel nitrate 6 aq and 18 g of 88% phosphoric acid in 200 ml of water. The resulting solution was divided into two equal portions which were applied for the impregnation of 175 g of the same alumina extrudates that were used for the preparation of catalyst I. The impregnation was effected in two steps, each with a portion of the afore-mentioned solution. After the first impregnation the alumina was dried at 120°C for two hours. After the second impregnation the alumina was dried at 120°C for two hours and calcined at 500°C for three hours.

The composition of the catalysts is given in Table A. Catalyst I is a catalyst according to the present selection invention.

TABLE A

Catalyst No.	Nickel content, gat/100 g Al_2O_3	Molybdenum content, gat/100 g Al_2O_3	Phosphorus content, gat/100 g Al_2O_3	Nickel/molybdenum atomic ratio
I	0.12	0.21	2.6	0.57:1
A	0.20	0.21	2.6	0.95:1
B	0.20	0.21	2.6	0.95:1
C	0.20	0.21	2.6	0.95:1
D	0.20	0.21	2.6	0.95:1

Hydrocracking Experiments

The temperature requirements, retentions of aromatics and selectivities of the catalysts mentioned in Table A, relating to the preparation of a lubricating oil with initial boiling point of 375°C and VI of 128 after dewaxing, were compared on the basis of an experiment carried out under the following circumstances.

Feed: propane-deasphalted short residue obtained after vacuum distillation of a crude oil originating from the Middle East.

VI of the de-asphalted oil after dewaxing at -20°C: 81

Sulphur content: 2.5 %w

Nitrogen content: 780 gdpn

Aromatics content: 100 mmol/100 g

Pressure: 150 kg/cm²

Space velocity: 1 l.l⁻¹.h⁻¹

Hydrogen/oil ratio: 2000 nl.l⁻¹

Catalyst bed: 100 ml.

The catalysts were crushed to a particle size of 0.5—1.4 mm and tested in sulphided form. Sulphiding was carried out by treating the catalysts for five hours with a mixture of

hydrogen and hydrogen sulphide in a volume ratio of 7:1 at a temperature of 375°C and a pressure of 10 kg/cm².

5 Dewaxing was carried out with a mixture of equal parts of methyl ethyl ketone and tol-

uene at -20°C, in which four parts by volume of the mixture were used to one part by volume of oil.

The results of this experiment are given in Table B.

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TABLE B

15	Applied catalyst	Temperature requirement, °C	Selectivity %w on feed	Properties of the lubricating oil		
				V _k 210°F, cS	Aromatics content, mmol/100 g	Retention of aromatics, %
15	I	420	45	9.4	27	27
	A	424	42	9.3	33	33
	B	428	39	8.8	40	40
	C	426	43	9.0	36	36
20	D	421	43	9.3	32	32

From the data given in Table B it appears that catalyst I, of which the atomic ratio of the metals A to the metals B is below 0.75:1, has a lower temperature requirement and retention of aromatics and a higher selectivity than the catalysts A—D, of which the atomic ratio of the metals A to the metals B is above the aforementioned limit (all catalysts contain the same quantity of metal B).

EXAMPLE 6

A residual fraction obtained from a North-African crude oil was deasphalted with the aid of liquid propane. The deasphalted residue had the following properties:

Specific weight 20/4: 0.907
Viscosity at 37°C: 32.8 cS
Viscosity index (VI_B, ASTM 2270) after dewaxing at -19°C: 77
40 Oil yield after dewaxing at -19°C: 89.2% by weight.

This deasphalted residual oil fraction was subjected to a catalytic hydrocracking treatment at the following conditions:

45 Temperature: 440°C
Pressure: 140 bars absolute
Space velocity: 1 kg of oil per hour per litre of catalyst
Hydrogen/oil ratio: 1000 litres (N.T.P.) per kg of oil.

The hydrocracking catalyst had the following composition:

	% by weight
55 Al ₂ O ₃	63.0
P ₂ O ₅	3.9
MoO ₃	19.4
NiO	9.7
F	3.0
SiO ₂	1.0

The fraction boiling below 400°C constituted 56% by weight of the hydrocracking product. It was separated off from the hydrocracking product by fractional distillation.

The fraction boiling above 400°C (44% wt) was dewaxed with the aid of a mixture of 50 parts by volume of methyl ethyl ketone and 50 parts by volume of toluene at a temperature of -27°C. The solvent/oil ratio was 3:1. During the dewaxing 12% by weight of slack wax was separated off. The luboil thus obtained had a viscosity index VI_B (ASTM—D 2270) of 130.

The yield of this luboil was 32% by weight calculated on the basis of the original deasphalted residual oil fraction.

The slack wax obtained in the dewaxing was then catalytically hydroisomerized applying the following conditions:

Temperature: 340°C
Pressure: 140 bars absolute
Space velocity: 0.81 kg of slack wax per hour per litre of catalyst
Hydrogen/slack wax ratio: 1.660 litres (N.T.P.) of hydrogen per kg of slack wax.

The hydroisomerization catalyst contained 17% by weight, tungsten, 9% by weight nickel and 2.5% by weight fluorine deposited on a support comprising 26% by weight alumina, the remainder being silica. This catalyst has been sulphurized by passing sulphur-containing gas oil thereover during 36 hours at the following conditions:

Temperature: 350°C
Pressure: 50 bars absolute
Space velocity: 1 kg of oil per hour per litre of catalyst
Hydrogen/oil ratio: 150 litres (N.T.P.) per kg of oil.

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By fractional distillation the fraction boiling below 400°C was separated from the hydroisomerization product. The yield of residue boiling above 400°C was 49.4% by weight calculated on the basis of the hydroisomerization feed. This residue was dewaxed at -27°C with the aid of a mixture of methyl ethyl ketone and toluene (50/50), the solvent/oil ratio being 8:1.

The yield of dewaxed luboil was 24.9% by weight calculated on the basis of the hydroisomerization feed.

This luboil has the following properties:
Viscosity index (VI_B, ASTM—D 2270): 158

Kinematic viscosity at 38°C: 30.60 cS
Kinematic viscosity at 99°C: 5.97 cS.

Comparative Experiment

A deasphalted residual oil fraction of the same origin and composition as the material used in Example 6 is dewaxed at -27°C with the aid of a mixture of methyl-ethylketone and toluene (50/50), the solvent/oil ratio being 3:1. In this operation 14% by weight slack wax is separated.

This slack wax is hydroisomerized at the same conditions and with the aid of the same sulphurized catalyst as mentioned in Example 6.

The fraction boiling above 400°C of the liquid hydroisomerization product is dewaxed in the same manner as mentioned in Example 6.

The yield of luboil is now 20% by weight calculated on the hydroisomerization feed. The luboil thus obtained had the following properties:

Viscosity index (VI_B, ASTM—D 2270): 100

Kinematic viscosity at 38°C: 295.3 cS
Kinematic viscosity at 99°C: 16.89 cS

EXAMPLE 7

A slack wax of the same composition as that obtained in the first dewaxing treatment of Example 6 was hydroisomerized with a catalyst which was identical with the hydrocracking catalyst used in Example 6.

The following conditions were applied:

Temperature: 400°C
Pressure: 140 bars absolute
Space velocity: 0.80 kg of slack wax per hour per litre of catalyst
Hydrogen/slack wax ratio: 1.780 litres (N.T.P.) of H₂ per kg of slack wax.

The fraction boiling below 400°C was separated by fractional distillation from the hydroisomerization product. The yield of residue boiling above 400°C was 61.2% by

weight calculated on the basis of the hydroisomerization feed.

This residue was dewaxed at -27°C with the aid of a mixture of methylethylketone and toluene (50/50), the solvent/oil ratio being 8:1. The luboil yield was 36.7% by weight calculated on the hydroisomerization feed. This luboil had the following properties:

Viscosity index (VI_B, ASTM—D 2270): 155

Kinematic viscosity at 38°C: 28.10 cS

Kinematic viscosity at 99°C: 5.60 cS.

WHAT WE CLAIM IS:—

1. A process for the preparation of a lubricating oil with a high viscosity index, characterized in that a high boiling mineral oil fraction is contacted at elevated temperature and pressure, in the presence of hydrogen, with a catalyst consisting of nickel and/or cobalt and molybdenum and/or tungsten, in metallic, oxidic and/or sulphidic form and of phosphorus oxide supported on a catalyst carrier consisting of refractory oxide.

2. A process according to claim 1, characterized in that the high boiling mineral oil fraction is a vacuum distillate boiling between 350°C and 550°C.

3. A process according to claim 1, characterized in that the high boiling mineral oil fraction is a deasphalted residual oil.

4. A process according to one or more of the preceding claims, characterized in that the temperature is between 400°C and 500°C, the pressure between 100 and 200 bars, the hourly space velocity between 0.1 and 10 kg of oil per hour per litre of catalyst and the hydrogen/oil ratio between 100 and 5000 standard litres of hydrogen per kg of oil.

5. A process according to one or more of the preceding claims, characterized in that the catalyst contains between 3% and 16% by weight of nickel and/or cobalt.

6. A process according to one or more of the preceding claims, characterized in that the catalyst contains 6 to 24% by weight of molybdenum and/or tungsten.

7. A process according to one or more of the preceding claims, characterized in that the catalyst contains between 1% and 12% by weight of phosphorus calculated as P₂O₅.

8. A process according to one or more of the preceding claims, characterized in that the catalyst contains between 2% and 9% of phosphorus calculated as P₂O₅.

9. A process according to one or more of the preceding claims, characterized in that the catalyst contains nickel.

10. A process according to one or more of the preceding claims, characterized in that the catalyst contains molybdenum.

11. A process according to one or more of the preceding claims, characterized in that

By fractional distillation the fraction boiling below 400°C was separated from the hydroisomerization product. The yield of residue boiling above 400°C was 49.4% by weight calculated on the basis of the hydroisomerization feed. This residue was dewaxed at -27°C with the aid of a mixture of methyl ethyl ketone and toluene (50/50), the solvent/oil ratio being 8:1.

The yield of dewaxed luboil was 24.9% by weight calculated on the basis of the hydroisomerization feed.

This luboil has the following properties:
Viscosity index (VI_E, ASTM—D 2270): 158

Kinematic viscosity at 38°C: 30.60 cS
Kinematic viscosity at 99°C: 5.97 cS.

Comparative Experiment

A deasphalted residual oil fraction of the same origin and composition as the material used in Example 6 is dewaxed at -27°C with the aid of a mixture of methyl-ethylketone and toluene (50/50), the solvent/oil ratio being 3:1. In this operation 14% by weight slack wax is separated.

This slack wax is hydroisomerized at the same conditions and with the aid of the same sulphurized catalyst as mentioned in Example 6.

The fraction boiling above 400°C of the liquid hydroisomerization product is dewaxed in the same manner as mentioned in Example 6.

The yield of luboil is now 20% by weight calculated on the hydroisomerization feed. The luboil thus obtained had the following properties:

Viscosity index (VI_E, ASTM—D 2270): 100

Kinematic viscosity at 38°C: 295.3 cS
Kinematic viscosity at 99°C: 16.89 cS

EXAMPLE 7

A slack wax of the same composition as that obtained in the first dewaxing treatment of Example 6 was hydroisomerized with a catalyst which was identical with the hydrocracking catalyst used in Example 6.

The following conditions were applied:

Temperature: 400°C
Pressure: 140 bars absolute
Space velocity: 0.80 kg of slack wax per hour per litre of catalyst
Hydrogen/slack wax ratio: 1.780 litres (N.T.P.) of H₂ per kg of slack wax.

The fraction boiling below 400°C was separated by fractional distillation from the hydroisomerization product. The yield of residue boiling above 400°C was 61.2% by

weight calculated on the basis of the hydroisomerization feed.

This residue was dewaxed at -27°C with the aid of a mixture of methylethylketone and toluene (50/50), the solvent/oil ratio being 8:1. The luboil yield was 36.7% by weight calculated on the hydroisomerization feed. This luboil had the following properties:—

Viscosity index (VI_E, ASTM—D 2270): 155

Kinematic viscosity at 38°C: 28.10 cS

Kinematic viscosity at 99°C: 5.60 cS.

WHAT WE CLAIM IS:—

1. A process for the preparation of a lubricating oil with a high viscosity index, characterized in that a high boiling mineral oil fraction is contacted at elevated temperature and pressure, in the presence of hydrogen, with a catalyst consisting of nickel and/or cobalt and molybdenum and/or tungsten, in metallic, oxidic and/or sulphidic form and of phosphorus oxide supported on a catalyst carrier consisting of refractory oxide.

2. A process according to claim 1, characterized in that the high boiling mineral oil fraction is a vacuum distillate boiling between 350°C and 550°C.

3. A process according to claim 1, characterized in that the high boiling mineral oil fraction is a deasphalted residual oil.

4. A process according to one or more of the preceding claims, characterized in that the temperature is between 400°C and 500°C, the pressure between 100 and 200 bars, the hourly space velocity between 0.1 and 10 kg of oil per hour per litre of catalyst and the hydrogen/oil ratio between 100 and 5000 standard litres of hydrogen per kg of oil.

5. A process according to one or more of the preceding claims, characterized in that the catalyst contains between 3% and 16% by weight of nickel and/or cobalt.

6. A process according to one or more of the preceding claims, characterized in that the catalyst contains 6 to 24% by weight of molybdenum and/or tungsten.

7. A process according to one or more of the preceding claims, characterized in that the catalyst contains between 1% and 12% by weight of phosphorus calculated as P₂O₅.

8. A process according to one or more of the preceding claims, characterized in that the catalyst contains between 2% and 9% of phosphorus calculated as P₂O₅.

9. A process according to one or more of the preceding claims, characterized in that the catalyst contains nickel.

10. A process according to one or more of the preceding claims, characterized in that the catalyst contains molybdenum.

11. A process according to one or more of the preceding claims, characterized in that





the catalyst carrier consists wholly or mainly of alumina.

12. A process according to claim 11, characterized in that the alumina contains between 0.5% and 3% by weight of silica and at most 0.005% by weight of sodium.

13. A process according to claim 12, characterized in that the catalyst carrier obtained by oxidation consists wholly or mainly of between 50% and 90% of silica and between 10% and 50% by weight of magnesia.

14. A process according to one or more of the preceding claims, characterized in that use is made of a catalyst prepared by impregnating a catalyst carrier with an aqueous solution of phosphoric acid, drying the impregnated carrier and impregnating it with an aqueous solution which contains a molybdate and a nickel salt and subsequently drying and calcining the impregnated carrier.

15. A process according to one or more claims 1 to 13, characterized in that use is made of a catalyst prepared by impregnating a catalyst carrier with an aqueous solution of a phosphomolybdate and/or of an acid phosphomolybdate and a nickel salt, and drying and calcining the impregnated carrier.

16. A process according to claim 14 or 15, characterized in that the nickel salt used is nickel hexamine dichloride or nickel formate.

17. A process according to claim 15 or 16, characterized in that the phosphomolybdate used is ammonium 2-phospho-5-molybdate $[(NH_4)_6(5MoO_3 \cdot 2PO_4) \cdot 7H_2O]$.

18. A process according to claim 15 or 16, characterized in that the acid phosphomolybdate used is ammonium 2-phospho-5-molybdate $[(NH_4)_6H(5MoO_3 \cdot 2PO_4) \cdot 6H_2O]$.

19. A process according to one or more of claims 14 to 18, characterized in that the solution of nickel salt and molybdate, phosphomolybdate and/or acid phosphomolybdate contains ammonium hydroxide.

20. A process according to one or more of the preceding claims, characterized in that the catalyst contains fluorine.

21. A process according to one or more of the preceding claims, characterized in that the catalyst contains between 1% and 6% by weight of fluorine.

22. A process according to one or more of the preceding claims, characterized in that the use is made of a sulphided catalyst.

23. A process as claimed in claim 20, characterized in that the catalyst is sulphided by contacting it with a sulphur compound containing oil at a temperature between 250°C and 450°C, a pressure between 30 and 70 bars, an hourly space velocity between 1 and 10 kg of oil per hour per litre of catalyst and a hydrogen/oil ratio of 50 to 500 standard litres of hydrogen per kg of oil.

24. A process according to one or more of the preceding claims, characterized in that

hydrocarbons boiling below a temperature in the range between 350°C and 400°C are distilled from the product of the catalytic hydrogenating treatment and that the higher boiling residue is dewaxed.

25. A process according to claim 4, characterized in that the dewaxing is effected by means of a mixture of methylethylketone and toluene, at a temperature between -10°C and -40°C and a volume ratio of solvent to oil between 1:1 and 10:1.

26. A process according to one or more of the preceding claims, characterized in that use is made of a catalyst containing at least one metal A chosen from the group formed by nickel and cobalt, at least one metal B chosen from the group formed by molybdenum and tungsten and also phosphorus on an oxidic catalyst carrier, the atomic ratio of the metals A to the metals B being below 0.75:1.

27. A process according to claim 26, characterized in that a catalyst is used in which the atomic ratio of the metals A to the metals B is between 0.2:1 and 0.65:1.

28. A process according to claim 26 or 27, characterized in that the preparation of the lubricating oil is carried out at a temperature of 375—425°C, a pressure of 100—200 kg/cm², a space velocity of 0.5—1.5 kg of feed per litre of catalyst per hour and a hydrogen/feed ratio of 500—2500 NI hydrogen per kg of feed.

29. A process according to one or more of claims 24 to 28, characterized in that the slack wax obtained in the dewaxing treatment is catalytically isomerized in the presence of a hydrogen-containing gas and that a luboil having a very high viscosity index is obtained by dewaxing the hydroisomerizate.

30. A process according to claim 29, characterized in that the hydroisomerization is carried out at a temperature in the range of from 310 to 450°C, a pressure in the range of from 50 to 200 bars absolute, a space velocity in the range of from 0.1 to 5.0 litres of slack wax per hour and per litre of catalyst and with a hydrogen/slack wax ratio in the from 100 to 5000 litres (N.T.P.) of hydrogen per kg of slack wax.

31. A process according to claim 29 or 30, characterized in that the hydroisomerization catalyst contains 0.5 to 40% by weight of a component having hydrogenation activity on an oxidic refractory carrier having cracking activity.

32. A process according to any one of claims 29—31, characterized in that the hydroisomerization catalyst contains 6 to 24% by weight tungsten and/or molybdenum and 3 to 18% by weight nickel and/or cobalt in the form of their oxides and/or sulphides.

33. A process according to any of claims 29—32, characterized in that the hydroisomerization catalyst support comprises a mix-

ture and/or a compound of silica and alumina, alumina and BF_3 , silica and magnesia, silica alumina and zirconia, alumina and P_2O_5 , or comprises a clay, which has been activated with acid, or a zeolite.

34. A process according to any one of claims 29—33, characterized in that the hydroisomerization catalyst contains 1 to 6% by weight of fluorine.

35. A process according to claim 29, characterized in that the hydroisomerization catalyst contains 3 to 18% by weight nickel, 6 to 24% by weight molybdenum, 1 to 6% by weight fluorine and 2 to 9% by weight of P_2O_5 deposited on a support consisting entirely or substantially of alumina.

36. A process according to claim 29, characterized in that the hydroisomerization catalyst contains platinum, alumina and 1 to 6% by weight fluorine.

37. A process according to any one of claims 29—36, characterized in that the portion boiling within the boiling range is separated by fractional distillation or flash distillation from the effluent of the hydroisomerization zone and is dewaxed, the slack wax thus obtained being recycled at least in part to the hydroisomerization zone.

38. A process according to any one of claims 29—37, characterized in that the hydrocracking treatment and the hydroiso-

merization are carried out with the same catalyst.

39. A process according to claim 38, characterized in that the hydrocracking treatment and the hydroisomerization are carried out consecutively in the same reactor.

40. A process according to claim 38 or 39, characterized in that the feed for the hydrocracking treatment consists of a blend of a high boiling mineral oil fraction and of slack wax obtained by dewaxing the portion of the product of the hydrocracking treatment and/or of the isomerization treatment which boils within the boiling range of luboil.

41. A process for the preparation of lubricating oil with a high viscosity index according to claim 1, as hereinbefore described with special reference to Examples 4 and 5.

42. A process for the preparation of lubricating oils with a very high viscosity index according to claim 29, as hereinbefore described with special reference to Examples 6 and 7.

43. Lubricating oils with high viscosity indices, whenever prepared by the process according to one or more of the preceding claims.

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