

PATENT SPECIFICATION

(11) 1 565 425

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- (21) Application No. 19268/77 (22) Filed 9 May 1977
 (31) Convention Application No. 7604955
 (32) Filed 10 May 1976 in
 (33) Netherlands (NL)
 (44) Complete Specification published 23 April 1980
 (51) INT CL³ C10G 47/10
 (52) Index at acceptance

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(54) PROCESS FOR THE MANUFACTURE OF LUBRICATING OIL

(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 manufacture of lubricating oil having a viscosity index above 140 by hydrocracking slack wax.

In United Kingdom Specifications 1,493,620 and 1,546,398 and in Netherlands patent application No. 7,602,603 in the name of the present Applicant, fluorine-containing catalysts have been described 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 at least 0.8 g/ml, comprise at least 3 parts by weight of nickel and/or cobalt, 10 parts by weight of molybdenum and 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 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, a further condition being that if in the catalyst preparation the starting material is an alumina hydrogel with a pore volume quotient of less than 0.5, 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. For a further description of the pore volume quotient reference is made to the above-mentioned United Kingdom patent specifications.

Unless otherwise stated all or part of the fluorine may be introduced into the catalyst by incorporating it into the alumina hydrogel or into the xerogel or by in situ fluoriding.

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.

As has been extensively demonstrated in the above-mentioned patent applications the catalysts described therein are eminently suitable for use in the preparation of high-viscosity-index lubricating oil by hydrocracking a mixture of heavy hydrocarbons, since they show, in addition to a very low temperature requirement and aromatic retention, a very high selectivity.

In a further investigation concerning the use of catalysts of this type, comprising at least 5 parts by weight of fluorine per 100 parts by weight of carrier, for lubricating oil manufacture by hydrocracking, it has been found

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that their suitability in the manufacture of lubricating oil with a viscosity index above 140 by hydrocracking slack wax having a nitrogen content below 500 ppmw (also called low-nitrogen slack wax), is even further enhanced when—by previous contact with basic nitrogen compounds present in atmospheric distillation residues of waxy crude oils—they have taken up at least 0.1 %w nitrogen.

The present patent application therefore relates to a process for the manufacture of lubricating oil having a viscosity index above 140 by hydrocracking slack wax having a nitrogen content of less than 500 ppmw using the aforementioned catalysts, which catalysts—by previous contact with basic nitrogen compounds present in atmospheric distillation residues of waxy crude oils—have taken up at least 0.1 %w nitrogen.

In lubricating oil manufacture according to the invention slack wax is used as the feed. Slack wax is obtained as a by-product in the manufacture of high-viscosity-index lubricating oil in the conventional way or by hydrocracking. The manufacture of high-viscosity-index lubricating oil in the conventional way is usually carried out as follows. An atmospheric distillation residue of a waxy crude oil is separated by distillation at reduced pressure into a number of distillate fractions (in particular one or more heavy gas oil, spindle oil, light machine oil and medium machine oil fractions) and a residue (called the "short residue"). From the lubricating oil fractions obtained by the distillation the corresponding lubricating oils are manufactured by refining. Refining of the spindle oil, light machine oil and medium machine oil fractions is effected by removal of at least part of the aromatics and paraffins from these fractions. In the refining of the "short residue" first of all asphalt is removed from the residue. Next, from the deasphalted oil thus obtained at least part of the aromatics and paraffins is removed. The residual lubricating oil thus manufactured is designated "bright stock". The manufacture of high-viscosity-index lubricating oil by hydrocracking is usually carried out as follows. A mixture of heavy hydrocarbons originating from a waxy crude oil, such as a vacuum distillate, a deasphalted oil or a slack wax is contacted at elevated temperature and pressure and in the presence of hydrogen with a suitable catalyst. From the product obtained in the hydrocracking (which product is sometimes subjected to hydrofinishing for quality improvement) the desired lubricating oil fractions are separated by distillation. The lubricating oil fractions obtained are refined by removal of at least part of the paraffins from these fractions.

The manufacture of lubricating oil having a viscosity index between 90 and 120 may be effected in the conventional way as well as by hydrocracking. For the manufacture of these

oils in the conventional way vacuum distillates as well as deasphalted oils are eligible as the feed. For the manufacture of these oils by hydrocracking a vacuum distillate is often used as the feed. For the manufacture of lubricating oil with a viscosity index above 120 only the hydrocracking route is suitable. For the manufacture of a lubricating oil with a viscosity index between 120 and 140 a deasphalted oil is often used as the feed. For the manufacture of lubricating oil with a viscosity index above 140 no other feed than slack wax is suitable.

In the lubricating oil manufacturing processes with waxy feeds as the starting material, described hereinbefore, finally dewaxing takes place, which reduces the pour point of the lubricating oil and renders it suitable for use at temperatures lower than ambient temperature. Dewaxing is usually effected by cooling the lubricating oil in the presence of a solvent. Dewaxing is preferably carried out with a mixture of methyl ethyl ketone and toluene at a temperature between -10 and -40°C and at a solvent/oil volume ratio between 1:1 and 10:1.

In the dewaxing of the lubricating oil fractions an oil-containing mixture of paraffins is obtained, which is referred to as "slack wax". The oil content of slack wax may vary within wide limits, depending on the way in which the dewaxing was carried out. As a rule, slack wax contains more than 5 and less than 40 %w oil. The nitrogen content of slack wax may also vary between wide limits and is dependent on the nitrogen contents of the paraffins and the oil present in the slack wax as well as on their mixing ratio. Slack wax obtained in the dewaxing of lubricating oil manufactured in the conventional way contains as a rule paraffins having a nitrogen content of about 50 ppmw and oil having a nitrogen content between 500 and 5000 ppmw. Slack wax obtained in the dewaxing of lubricating oil manufactured by hydrocracking as a rule contains paraffins whose nitrogen content is only a few ppmw and oil having a nitrogen content of less than 100 ppmw. In view of the above it may generally be stated that slack wax obtained in the dewaxing of lubricating oil manufactured by hydrocracking will practically always have a nitrogen content of less than 500 ppmw, whereas slack wax obtained in the dewaxing of lubricating oil manufactured in the conventional way will have such a low nitrogen content only in some cases. The present patent application relates to the manufacture of lubricating oil by hydrocracking such low-nitrogen slack wax.

In the process according to the invention the catalyst is made to take up at least 0.1 %w nitrogen by contact with certain nitrogen compounds. This nitrogen uptake can be realized in various ways.

In the first place the nitrogen compounds

concerned may be added continuously to the low-nitrogen slack wax in the initial stage of lubricating oil manufacture, this addition being continued until the nitrogen content of the catalyst is at least 0.1 %w. The lubricating oil manufacturing process is subsequently continued without addition of nitrogen compounds. A drawback of this embodiment is that the nitrogen compounds concerned must be available as such, and therefore must first be separated from a suitable distillation residue. This separation may present problems. Preference is therefore given to a process in which a suitable distillation residue or a fraction thereof containing a sufficient quantity of the nitrogen compounds concerned is continuously added to the low-nitrogen slack wax during the initial stage of lubricating oil manufacture, this addition being continued until the nitrogen content of the catalyst is at least 0.1 %w. The lubricating oil manufacturing process is subsequently continued without addition of the nitrogen-containing oil fraction. The amount of nitrogen compounds which, as such or in the form of a nitrogen-containing oil fraction, has to be added continuously to the low-nitrogen slack wax during the initial stage of the lubricating oil manufacture, should be such that during this period the nitrogen content of the slack wax to be processed is at least 500 ppmw and preferably more than 1000 ppmw.

Another possibility of realising the desired nitrogen uptake by the catalyst consists in processing, prior to the low-nitrogen slack wax, first a slack wax having a nitrogen content of at least 500 ppmw and preferably more than 1000 ppmw until the nitrogen content of the catalyst is at least 0.1 %w and that thereupon the lubricating oil manufacturing process is continued using the low-nitrogen slack wax as the feed.

A very attractive embodiment of the process according to the invention is based on the following considerations:

- A) The required nitrogen compounds occur in atmospheric distillation residues of waxy crude oils.
- B) Fractions of these distillation residues are used as the feed for the manufacture of a high-viscosity-index lubricating oil by hydrocracking.
- C) The present catalysts are pre-eminently suitable for the use mentioned under B.

On the basis of considerations A—C the process according to the invention is preferably carried out as follows. A catalyst of the present type is used for the manufacture of lubricating oil having a viscosity index between 90 and 140 by hydrocracking a vacuum distillate or deasphalted oil having a nitrogen content of at least 500 ppmw, and preferably of more than 1000 ppmw, which feed has been obtained from an atmospheric distillation residue of a waxy crude oil. After the catalyst

has taken up at least 0.1 %w nitrogen while this feed is being processed, the feed is replaced by slack wax having a nitrogen content of less than 500 ppmw and the lubricating oil manufacture is continued, now for the manufacture of a lubricating oil having a viscosity index above 140.

The above-described embodiment of the process according to the invention in which the catalyst is first used for the manufacture of lubricating oil having a viscosity index between 90 and 140 and then for the manufacture of lubricating oil having a viscosity index above 140 is very suitable for use in a combined process for lubricating oil manufacture, in which the slack wax obtained in dewaxing the lubricating oil manufactured by hydrocracking and having a viscosity index between 90 and 140, is used as the feed in the subsequent manufacture of lubricating oil having a viscosity index above 140. A process for lubricating oil manufacture on a commercial scale with application of the process according to the invention may very suitably be effected by using a catalyst of the present type several times and alternately for the manufacture of a lubricating oil having a viscosity index between 90 and 140 and thereupon for the manufacture of a lubricating oil having a viscosity index above 140 in such a manner that the first time the process is used for the manufacture of lubricating oil having a viscosity index above 140, the starting material is slack wax obtained in the dewaxing of lubricating oil having a viscosity index between 90 and 140 prepared previously, whilst on subsequent occasions where the process is used for the manufacture of lubricating oil having a viscosity index above 140 an additional feed component is slack wax obtained in the dewaxing of lubricating oil having a viscosity index above 140, manufactured in a previous stage of the process.

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/

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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 fluorine present in the catalysts used according to the invention is preferably 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.

Hydrocracking a slack wax for the manufacture of lubricating oil having a viscosity index above 140 according to the invention is effected by contacting the slack wax at elevated temperature and pressure and in the presence of hydrogen with the catalyst, which is preferably present in one or more beds of particles having a size between 0.5 and 3 mm.

Suitable hydrocracking conditions are: a temperature of from 325° to 450°C, a pressure of from 10 to 250 bar, a hydrogen/feed ratio of from 100 to 5000 NI of hydrogen per kg of feed and a space velocity of from 0.2 to 5.0 kg of feed per litre of catalyst per hour. It is preferable to employ the following conditions: a temperature of from 350 to 425°C, a pressure of from 100 to 200 bar, a hydrogen/feed ratio of from 500 to 2500 NI of hydrogen per kg of feed and a space velocity of from 0.5 to 1.5 kg of feed per litre of catalyst per hour.

The invention will now be elucidated with reference to the following examples.

Six catalysts were used for the manufacture of lubricating oil having a viscosity index above 140 by hydrocracking five feeds. The preparation of the catalysts and the properties of the feeds are given hereinafter.

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 by the hydrogel route. For the preparation of catalysts 1 and 2 the starting material was an alumina hydrogen 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). For the preparation of catalysts 3 and 4 the starting material was an alumina hydrogel from which, by drying and calcining, a xerogel could be obtained with a compacted

bulk density of 0.7 g/ml and a pore volume quotient of 0.3 (alumina hydrogel II).

The preparation of catalysts 1, 3 and 4 was effected by mixing an aqueous solution containing a nickel, a tungsten and a fluorine compound with either alumina hydrogel I (for the preparation of catalyst 1), or alumina hydrogel II (for the preparation of catalysts 3 and 4) and maintaining the mixture for some time at elevated temperature, separating the metal-loaded hydrogel from the mixture and then drying, extruding and calcining it. In the preparation of catalysts 3 and 4 100 and 75%, respectively, of the quantity of fluorine present on the ready catalysts was incorporated into the hydrogel. The pore volume quotients of the xerogels which could be obtained from these fluorine-containing hydrogels by drying and calcining were 0.7 and 0.6, respectively. The additional quantity of fluorine (25%) was incorporated into catalyst 4 by in-situ fluoriding. The compacted bulk densities of catalysts 1, 3 and 4 were 1.2, 1.4, and 1.5 g/ml, respectively.

The preparation of catalyst 2 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 elevated temperature, separating the metal-loaded hydrogel from the mixture and then drying, extruding and calcining it. Fluorine was incorporated into catalyst 2 by in-situ fluoriding. The compacted bulk density of catalyst 2 was 1.5 g/ml.

Catalysts 5 and 6

Per 100 parts by weight of alumina, these catalysts both comprised 5 parts by weight of nickel and 30 parts by weight of tungsten. Catalysts 5 and 6 comprised, in addition, 6 and 10 parts by weight, respectively, of fluorine per 100 parts by weight of alumina. They were prepared by the xerogel route. For the preparation of catalyst 5 the starting material was alumina hydrogel I. 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 0.70 g/ml and a pore volume quotient of 0.25 (alumina hydrogel III).

The preparation of catalyst 5 was effected by drying, extruding and calcining alumina hydrogel I, impregnating the extrudates with an aqueous solution comprising a nickel and a tungsten compound, and drying and calcining the impregnated extrudates. Fluorine was incorporated into catalyst 5 by in-situ fluoriding.

The preparation of catalyst 6 was effected by mixing an aqueous solution containing a fluorine compound with alumina hydrogel III, maintaining the mixture for some time at elevated temperature, separating the fluorine-

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loaded hydrogel from the mixture, and then 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 catalyst 6 60% of the quantity of fluorine present on the ready catalyst was incorporated into the hydrogel. The pore volume quotient of the xerogel that could be prepared from this fluorine-containing hydrogel by drying and calcining was 0.7. The additional quantity of fluorine (40%) was incorporated into catalyst 6 by in-situ fluoriding. The compacted bulk densities of catalysts 5 and 6 were 0.9 and 1.2 g/ml, respectively.

Feed I

Slack wax obtained in the dewaxing of a residual lubricating oil manufactured in the conventional way.

Properties of the slack wax:

Oil content	5.6	%w
Sulphur content	0.52	%w
Nitrogen content	81	ppmw

Feed II

Slack wax obtained in the dewaxing of a residual lubricating oil manufactured in the conventional way from a waxy crude oil.

Properties of the slack wax:

Oil content	29.3	%w
Sulphur content	0.71	%w
Nitrogen content	97	ppmw

Feed III

Slack wax obtained in the dewaxing of a residual lubricating oil manufactured by hydrocracking/hydrofinishing.

Properties of the slack wax:

Oil content	5.3	%w
Sulphur content	15	ppmw
Nitrogen content	4	ppmw

Feed IV

Mixture of slack wax obtained in the dewaxing of distillate and residual lubricating oils manufactured by hydrocracking.

Properties of the slack wax mixture:

Oil content	20	%w
Sulphur content	0.3	%w
Nitrogen content	95	ppmw

Feed V

Slack wax obtained in the dewaxing of a lubricating oil having a viscosity index of 95, which had been manufactured by hydrocracking over catalyst 1 the medium machine oil further described hereinafter.

Properties of the slack wax:

Oil content	27.4	%w
Sulphur content	0.18	%w
Nitrogen content	<1	ppmw

EXAMPLE

The influence of the aforementioned uptake of nitrogen by catalysts 1—6 in the manufacture of 390°C+ lubricating oils having a viscosity index of about 150 after dewaxing at -30°C, was examined in hydrocracking experiments with feeds I—V. The hydrocracking was carried out under the following conditions, 70 %w of the slack wax being converted:

Hydrogen partial

pressure	130 bar	70
Space velocity	1 kg . l ⁻¹ . h ⁻¹	
Hydrogen/feed ratio	1500 Nl . kg ⁻¹	

With each of feeds I—V and each of catalysts 1—6 two hydrocracking experiments were carried out; one with the fresh catalyst and the other with the catalyst after it had been used for 750 hours in hydrocracking a medium machine oil (MMO) fraction originating from a waxy crude oil and having a nitrogen content of 1200 ppmw and a sulphur content of 2.5 %w. Hydrocracking of the MMO was effected under the following conditions:

Temperature	380—400°C	
Hydrogen partial pressure	1 kg . l ⁻¹ . h ⁻¹	85
Hydrogen/feed ratio	2000 Nl . kg ⁻¹	

The catalysts were employed in sulphided form. Sulphiding of the catalysts was carried out by contacting them for 5 hours with a mixture of hydrogen and hydrogen sulphide in a volume ratio of 7:1 at a temperature between 75 and 375°C and a pressure of 10 bar. De-waxing was effected using a mixture of methyl ethyl ketone and toluene in a ratio of 1:1. In-situ fluoriding of eligible catalysts was effected by adding 300 ppmw of fluorine in the form of ortho-fluorotoluene to the feed during the initial stage of the test until the required fluorine content of the catalyst had been reached.

The catalysts were used in the form of 1.5 mm extrudates.

In all experiments with the fresh catalysts the nitrogen content of the catalysts at run hour 750 (so after the slack wax had been hydrocracked for 750 hours) was less than 0.1 %w.

The results of the experiments are collected in Table A.

The yields mentioned in the last column were in each experiment measured between run hours 750 and 760.

TABLE A

	Exp. No.	Cat. No.	Feed No.	Exp. with fresh cat.	Exp. with aged cat.	Nitrogen content of cat. after 750 h hydrocracking of MMO, %w	Yield of luboil with VI of about 150, %w
5	1	1	I		+	0.12	40
10	1'	1	I	+			30
	2	1	II		+	0.14	38
	2'	1	II	+			32
	3	2	I		+	0.11	37
	3'	2	I	+			26
15	4	2	II		+	0.13	35
	4'	2	II	+			30
	5	3	I		+	0.15	39
	5'	3	I	+			30
	6	3	II		+	0.16	37
20	6'	3	II	+			32
	7	4	I		+	0.16	38
	7'	4	I	+			28
	8	4	II		+	0.16	37
	8'	4	II	+			31
25	9	5	I		+	0.10	43
	9'	5	I	+			32
	10	5	II		+	0.11	38
	10'	5	II	+			30
	11	6	I		+	0.12	42
30	11'	6	I	+			33
	12	6	II		+	0.13	37
	12'	6	II	+			30
	13	1	III		+	0.16	45
	13'	1	III	+			25
35	14	2	III		+	0.15	44
	14'	2	III	+			23
	15	5	III		+	0.15	47
	15'	5	III	+			22
	16	6	III		+	0.17	45
40	16'	6	III	+			20
	17	1	IV		+	0.13	39
	17'	1	IV	+			32
	18	5	IV		+	0.15	40
	18'	5	IV	+			30
45	19	1	V		+	0.12	47
	19'	1	V	+			25

Of the experiments mentioned in Table A Nos. 1—18' were carried out without gas recirculation in a 250 ml reactor and Nos. 19 and 19' with gas recirculation in a 2 l reactor.

Experiment 19 is an example of the combined process for lubricating oil manufacture described in the specification. In this experiment a catalyst of the present type was first used for the manufacture of lubricating oil having a viscosity index between 90 and 140 (95) by hydrocracking a vacuum distillate having a nitrogen content of at least 500 ppmw (1200) and subsequently, after the catalyst had thereby taken up at least 0.1 (0.12) %w nitrogen, the slack wax separated from this lubricating oil by dewaxing, was used as

feed for the manufacture of lubricating oil having a viscosity index above 140 (about 150) by hydrocracking over the catalyst aged in this way.

WHAT WE CLAIM IS:—

1. A process for the manufacture of lubricating oil having a viscosity index above 140 by hydrocracking slack wax having a nitrogen content of less than 500 ppmw, characterized in that fluorine-containing catalysts are used 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 at least 0.8 g/ml, comprise at least 5 parts by weight of fluorine,

TABLE A

	Exp. No.	Cat. No.	Feed No.	Exp. with fresh cat.	Exp. with aged cat.	Nitrogen content of cat. after 750 h hydrocracking of MMO, %w	Yield of lubeoil with VI of about 150, %w
5	1	1	I		+	0.12	40
10	1'	1	I	+			30
	2	1	II		+	0.14	38
	2'	1	II	+			32
	3	2	I		+	0.11	37
	3'	2	I	+			26
15	4	2	II		+	0.13	35
	4'	2	II	+			30
	5	3	I		+	0.15	39
	5'	3	I	+			30
	6	3	II		+	0.16	37
20	6'	3	II	+			32
	7	4	I		+	0.16	38
	7'	4	I	+			28
	8	4	II		+	0.16	37
	8'	4	II	+			31
25	9	5	I		+	0.10	43
	9'	5	I	+			32
	10	5	II		+	0.11	38
	10'	5	II	+			30
	11	6	I		+	0.12	42
30	11'	6	I	+			33
	12	6	II		+	0.13	37
	12'	6	II	+			30
	13	1	III		+	0.16	45
	13'	1	III	+			25
35	14	2	III		+	0.15	44
	14'	2	III	+			23
	15	5	III		+	0.15	47
	15'	5	III	+			22
40	16	6	III		+	0.17	45
	16'	6	III	+			20
	17	1	IV		+	0.13	39
	17'	1	IV	+			32
	18	5	IV		+	0.15	40
	18'	5	IV	+			30
45	19	1	V		+	0.12	47
	19'	1	V	+			25

Of the experiments mentioned in Table A Nos. 1—18^a were carried out without gas recirculation in a 250 ml reactor and Nos. 19 and 19' with gas recirculation in a 2 l reactor.

Experiment 19 is an example of the combined process for lubricating oil manufacture described in the specification. In this experiment a catalyst of the present type was first used for the manufacture of lubricating oil having a viscosity index between 90 and 140 (95) by hydrocracking a vacuum distillate having a nitrogen content of at least 500 ppmw (1200) and subsequently, after the catalyst had thereby taken up at least 0.1 (0.12) %w nitrogen, the slack wax separated from this lubricating oil by dewaxing, was used as

feed for the manufacture of lubricating oil having a viscosity index above 140 (about 150) by hydrocracking over the catalyst aged in this way.

WHAT WE CLAIM IS:—

1. A process for the manufacture of lubricating oil having a viscosity index above 140 by hydrocracking slack wax having a nitrogen content of less than 500 ppmw, characterized in that fluorine-containing catalysts are used 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 at least 0.8 g/ml, comprise at least 5 parts by weight of fluorine,



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3 parts by weight of nickel and/or cobalt, 10 parts by weight of molybdenum and 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 hydrogen, 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, a further condition being that if in the catalyst preparation the starting material is an alumina hydrogel with a pore volume quotient of less than 0.5, 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 and that the catalysts that are used, by previous contact with basic nitrogen compounds present in atmospheric distillation residues of waxy crude oils, have taken up at least 0.1 %w nitrogen.

2. A process according to claim 1, characterized in that the nitrogen compounds concerned or a distillation residue or a fraction thereof containing a sufficient quantity of the nitrogen compounds concerned, is continuously added to the low-nitrogen slack wax during the initial stage of lubricating oil manufacture, until the nitrogen content of the catalyst is at least 0.1 %w and that the lubricating oil manufacturing process is subsequently continued without addition of nitrogen compounds or nitrogen-containing oil fraction.

3. A process according to claim 2, characterized in that such an amount of the nitrogen compounds concerned or of an oil fraction containing these nitrogen compounds is added

to the low-nitrogen slack wax during the initial stage of the lubricating oil manufacture, that during this period the nitrogen content of the slack wax to be processed is more than 1000 ppmw.

4. A process according to claim 1, characterized in that prior to the processing of the low-nitrogen slack wax, first a slack wax is processed having a nitrogen content of at least 500 ppmw and preferably more than 1000 ppmw until the nitrogen content of the catalyst is at least 0.1 %w and that thereupon the lubricating oil manufacturing process is continued using the low-nitrogen slack wax as the feed.

5. A process according to claim 1, characterized in that a catalyst of the present type is used for the manufacture of lubricating oil having a viscosity index between 90 and 140 by hydrocracking a vacuum distillate or deasphalted oil having a nitrogen content of at least 500 ppmw, and preferably of more than 1000 ppmw, which feed has been obtained from an atmospheric distillation residue of a waxy crude oil and that after the catalyst has taken up at least 0.1 %w nitrogen while this feed is being processed, the feed is replaced by a slack wax having a nitrogen content of less than 500 ppmw and the lubricating oil manufacture is continued, now for the manufacture of a lubricating oil having a viscosity index above 140.

6. A process according to claim 5, characterized in that slack wax obtained in dewaxing the lubricating oil manufactured by hydrocracking and having a viscosity index between 90 and 140, is used as the feed in the subsequent manufacture of lubricating oil having a viscosity index above 140.

7. A process according to claim 6, characterized in that a catalyst of the present type is used several times alternately, first for the manufacture of lubricating oil having a viscosity index between 90 and 140 and thereupon for the manufacture of lubricating oil having a viscosity index above 140 and that the first time the process is used for the manufacture of lubricating oil having a viscosity above 140, the starting material is slack wax obtained in the dewaxing of lubricating oil having a viscosity index between 90 and 140 prepared previously, whilst on subsequent occasions where the process is used for the manufacture of lubricating oil having a viscosity index above 140 an additional feed component is slack wax obtained in the dewaxing of lubricating oil having a viscosity index above 140, manufactured in a previous stage of the process.

8. A process according to any one of claims 1-7, 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

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of tungsten per 100 parts by weight of alumina.

5 9. A process according to claim 8, characterized in that a catalyst is employed in which the nickel-to-tungsten weight ratio is between 1:5 and 1:7.

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

15 11. A process according to any one of claims 1-7, characterized in that a catalyst is employed which has been prepared by the hydrogel route and comprises 25-80 parts by weight of nickel and 50-80 parts by weight of tungsten per 100 parts by weight of alumina.

20 12. A process according to claim 11, characterized in that a catalyst is employed in which the nickel-to-tungsten weight ratio is between 1:1.5 and 1:5.

25 13. A process according to any one of claims 1-7, 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.

30 14. A process according to claim 13, 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.

35 15. A process according to any one of claims 1-7 and 11-14, 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.

40 16. A process according to any one of claims 1-15, characterized in that this is carried out at a temperature of from 325° to 450°C and preferably of from 350° to 425°C, a pressure of from 10 to 250 bar and preferably of from 100 to 200 bar, a space velocity of from 0.2 to 5 kg. l⁻¹. h⁻¹ and preferably of from 0.5 to 15 kg. l⁻¹. h⁻¹ and a hydrogen/feed ratio of from 100 to 5000 NI. kg⁻¹ and preferably of from 500 to 2500 NI. kg⁻¹.

50 17. A process for the manufacturing of lubricating oil having a viscosity index above 140, substantially as described hereinbefore and in particular with reference to experiments 1-19 of the example.

55 18. Lubricating oils having a viscosity index above 140 manufactured according to a process as described in claim 17.

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