

PATENT SPECIFICATION

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(54) PROCESS FOR THE PREPARATION OF TECHNICAL WHITE OILS AND MEDICINAL OILS

(71) We, SHELL INTERNATIONAL 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 patent application relates to a process for the preparation of technical white oils. In this patent application by technical white oils is understood hydrocarbon oils which are almost odourless and tasteless, which possess a Saybolt colour greater than +30 and which meet the F.D.A. No. 121,2589 specification. According to this specification the UV absorption of the oil in the wavelength regions 280—289 nm, 290—299 nm, 300—329 nm and 330—350 nm should amount to at most 4.0, 3.3, 2.3 and 0.8, respectively.

Among the various fields in which technical white oils are extensively used are the textile, plastics, cosmetic, paper and rubber industries. They are prepared, for instance, from a hydrocarbon mixture with a suitable viscosity as the starting material by successively treating this mixture with a large quantity of concentrated sulphuric acid, neutralizing it and treating it with clay. This process has a number of drawbacks. The principal drawback concerns the waste products obtained in the process, consisting of acid tar and spent clay. In view of the tightening of requirements imposed by environmental control, the disposal of the considerable quantities of these waste products obtained in this process becomes increasingly difficult. Another drawback of the above-mentioned process is the yield. Depending on the quantity of undesired constituents which are present in the starting material, and which are removed in the various refining steps, the process may lead to a relatively low yield of technical white oil. Finally, the process is rather expensive.

In order to obviate the above-mentioned

drawbacks of the preparation of technical white oils, it has already been proposed to prepare these oils via a catalytic treatment with hydrogen. To this end a hydrocarbon mixture with a suitable viscosity is brought into contact with a catalyst at elevated temperature and pressure and in the presence of hydrogen. Since in this process no large quantity of concentrated sulphuric acid is used and consequently no considerable quantity of acid tar is formed either, the problem of waste products hardly plays a part in this process. Since, in addition, undesired constituents which are present in the starting material are converted into valuable technical white oil components, instead of being removed, this process leads to a considerably higher yield of technical white oil than the afore-mentioned process via treatment with a large quantity of concentrated sulphuric acid. Finally, the process is much less expensive.

In the preparation of technical white oils via a catalytic treatment with hydrogen, the activity of the catalyst plays a very important part. If the catalyst has a lower activity a higher temperature has to be applied to reach the desired conversion. Higher temperatures favour cracking reactions as a result of which the yield of technical white oil decreases and the hydrogen consumption increases. In addition, higher temperatures promote the formation of structures which adversely affect the results of the test according to F.D.A. No. 121,2589. Consequently, in a number of cases it appears that technical white oils prepared via a catalytic treatment with hydrogen do not yet completely meet the specifications formulated in this patent application for technical white oils, so that an additional light acid and/or clay treatment has to be applied to bring these oils on specification.

It has now been found that technical white oils which completely meet the specifications formulated in this patent application without an additional acid and/or clay treatment being necessary, can be prepared in high yield by catalytic treatment with hydrogen of a hydrocarbon mixture, provided that the follow-

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ing conditions are fulfilled. In the treatment with hydrogen, which is carried out at a temperature between 275 and 375° C, the hydrocarbon mixture has to be converted into a liquid product consisting to an extent of less than 30 %w of components with a boiling point lower than the initial boiling point of the feed. Furthermore, the catalyst applied in the treatment with hydrogen has to be a fluorine containing sulphidic catalyst containing nickel and/or cobalt and, in addition, molybdenum and/or tungsten on a carrier and in which at least part of the fluorine is taken up by in-situ fluorination. From the product obtained in the treatment with hydrogen the desired technical white oil is isolated by topping off light components. It has further been found that in a number of cases the oils prepared in this way not only meet the specifications formulated in this patent application for technical white oils, but also the specification according to F.D.A. No. 121,1146. According to this specification, which forms part of the specifications which medicinal oils should meet in general, the UV absorption of the oil in the wavelength region 260—350 nm must amount to at most 0.10.

The process according to the invention in which the catalytic treatment with hydrogen is carried out in such a way that the hydrocarbon starting material is converted into a liquid product consisting to an extent of less than 30%w of components with a boiling point lower than the initial boiling point of the feed, clearly differs from known processes for the preparation of lubricating oils with a high viscosity index by the catalytic hydrocracking of hydrocarbon mixtures in which the hydrocarbon starting material is converted into a liquid product mostly consisting to an extent of more than 50%w of components with a boiling point lower than the initial boiling point of the feed.

The present patent application therefore relates to a process for the preparation of technical white oils, in which a hydrocarbon mixture is converted into a liquid product consisting to an extent of less than 30%w of components with a boiling point lower than the initial boiling point of the feed by a treatment with hydrogen at a temperature between 275 and 375° C in the presence of a fluorine-containing sulphidic catalyst containing nickel and/or cobalt and, in addition, molybdenum and/or tungsten on a carrier and in which at least part of the fluorine has been incorporated by in-situ fluorination, and in which from the product obtained in the treatment with hydrogen the desired technical white oil is isolated by topping off light components.

In the process according to the invention it is of vital importance that a fluorine-containing catalyst is applied in which at least part of the fluorine is taken up by in-situ

fluorination. Incorporation of fluorine into catalysts can in principle be carried out in two ways. Fluorine can be incorporated into catalysts by impregnating them during or after the preparation with a suitable fluorine compound such as ammonium fluoride. It is also possible to incorporate fluorine into catalysts during the process for which the catalyst is applied by adding a suitable fluorine compound to the gas and/or liquid stream which is passed over the catalyst. If desired, the last-mentioned fluorination technique, which is usually referred to as in-situ fluorination may be combined with the impregnation technique mentioned before. For example, part of the required quantity of fluorine can be incorporated into the catalyst by impregnation during the preparation and the remainder by in-situ fluorination during the process for which the catalyst is applied.

The present catalysts into which fluorine is incorporated by in-situ fluorination are considerably more suitable for the preparation of technical white oils via a treatment with hydrogen than catalysts with the same metal load containing no fluorine. That this must at least partly be attributed to the way in which fluorine is incorporated into the catalyst is shown by the fact that the present catalysts into which fluorine has been incorporated by in-situ fluorination are also considerably more suitable for the preparation of technical white oils via a treatment with hydrogen than catalysts with the same metal load and the same fluorine content into which fluorine has been incorporated by impregnation.

In addition to an excellent suitability of the present catalysts for the preparation of technical white oils via a treatment with hydrogen, the use of in-situ fluorinated catalysts for this purpose offers additional advantages. As opposed to in-situ fluorination, which can easily take place during the treatment with hydrogen, fluorination by impregnation requires special facilities which, as a rule, are not available in a plant for the preparation of technical white oils. Since for the optimum conversion of feeds with different compositions, catalysts with different fluorine contents have to be applied, it has up to now been necessary to have a number of catalysts with different fluorine contents available for the conversion of these feeds. The present invention is therefore very important from a point of view of economy, since it offers a possibility of converting feeds with strongly different compositions with only one base catalyst which is fluorine-free or has a low fluorine content. By in-situ fluorination the fluorine content of the catalyst can be adapted to the composition of the feed. In-situ fluorination offers in addition the possibility of increasing the fluorine content of the catalyst during the process in proportion as the catalyst is deactivated.

As was mentioned hereinbefore, in-situ fluorination can be carried out by adding a suitable fluorine compound to the gas and/or liquid stream which is passed over the catalyst. In-situ fluorination is preferably carried out in such a way that almost all the fluorine which is added to the gas and/or liquid stream is taken up by the catalyst. For this purpose an organic fluorine compound is preferably chosen. Examples of suitable fluorine compounds are ortho-fluorotoluene, difluoroethane, difluoroethene and trifluoroethane.

The total amount of fluorine that has to be added to the gas and/or liquid stream depends on the quantity of catalyst to be fluorinated and on the required fluorine content of the catalyst. For the preparation of technical white oils from a hydrocarbon mixture via a treatment with hydrogen catalysts are preferably chosen which contain 0.5—25 parts by weight and particularly 1—10 parts by weight of fluorine per 100 parts by weight of carrier. If it is assumed that all the fluorine which is added to the gas and/or liquid stream is taken up by the catalyst, the total quantity of fluorine that has to be added can easily be calculated. If the concentration of the fluorine compound in the gas and/or liquid stream is higher, the time required for in-situ fluorination is shorter. During in-situ fluorination the catalyst properties change and consequently also the composition of the product leaving the reactor. In order to reach stable operation as soon as possible, in-situ fluorination should take place in a short period of time. This can be achieved by application of a high concentration of the fluorine compound in the gas and/or liquid stream during in-situ fluorination. On the other hand, the concentration of the fluorine compound should not be chosen too high, since then there would be a fair chance of part of the quantity of fluorine added not being taken up by the catalyst, but ending up in the product leaving the reactor. During the part of the process in which the catalyst is fluorinated in-situ, preferably a quantity of 20—5000 ppmw and in particular 30—2000 ppmw of fluorine is added to the gas and/or liquid stream in the form of a fluorine compound.

In-situ fluorination of the catalyst is preferably carried out at an early stage of the treatment with hydrogen, for instance during or after starting up the process. If desired, in-situ fluorination of the catalyst can also be carried out at a later stage of the process.

Though in-situ fluorinated catalysts of the present type as such show a high stability when used for the preparation of technical white oils from hydrocarbon mixtures via a treatment with hydrogen, the stability of these catalysts can be further increased by continuously adding, during the process, a small quantity of a fluorine compound to the gas

and/or liquid stream, after the required quantity of fluorine has been applied onto the catalyst by in-situ fluorination. Quantities of 1—50 ppmw and in particular of 5—25 ppmw of fluorine in the form of a fluorine compound are very suitable for this purpose. The fluorine compound applied may be the same as the used for in-situ fluorination or may be different.

At least part of the fluorine present in the catalysts that are applied in the preparation of technical white oils according to the invention should be incorporated therein by in-situ fluorination. Preference is given to catalysts in which more than 50% of the fluorine and in particular to catalysts in which virtually all of the fluorine has been incorporated by in-situ fluorination.

The catalysts applied in the process according to the invention are fluorine-containing sulphidic catalysts containing nickel and/or cobalt and, in addition, molybdenum and/or tungsten on a carrier. Preference is given to catalysts containing 1—30 parts by weight and in particular 2—20 parts by weight of nickel and/or cobalt and 1—80 parts by weight and in particular 10—80 parts by weight of molybdenum and/or tungsten per 100 parts by weight of carrier. The weight ratio of nickel and/or cobalt on the one hand to molybdenum and/or tungsten on the other preferably lies between 1:1 and 1:10. Besides nickel and/or cobalt, molybdenum and/or tungsten and fluorine, the catalysts applied in the process according to the invention may contain promoters such as boron and phosphorus.

Examples of suitable carriers for the present catalysts are amorphous oxides of the elements of the Groups II, III and IV of the Periodic System, such as silica, alumina, magnesia, zirconia, thorina and boria, as well as mixtures of these oxides such as silica-alumina, silica-magnesia, silica-zirconia and silica-alumina-zirconia. Preference is given to catalysts containing alumina as a carrier. Further, preference is given to catalysts with a surface area of 50—500 m²/g and a pore volume of 0.2—1.0 ml/g.

The metals can be incorporated in the present catalysts according to any process known in the art for the preparation of catalysts containing several components on a carrier, for instance by co-impregnation of a carrier in one or more steps with an aqueous solution containing salts of the metals concerned, followed by drying and calcination. If the impregnation is carried out in several steps the material can be dried and calcined between the various impregnation steps.

In the process according to the invention catalysts are applied of which the catalytically active metals are in the sulphidic form. Sulphiding of the catalysts can take place according to any process known in the art for

the sulphiding of catalysts. Sulphiding can take place, for instance, by bringing the catalyst into contact 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. Sulphiding can also be carried out by bringing the catalyst into contact with hydrogen and a sulphur-containing hydrocarbon oil, such as a sulphur-containing kerosine or gas oil. If in the process according to the invention a feed is applied with a low sulphur content, it is recommended that during the process a small quantity of a sulphur compound be continuously added to the feed, in order to ensure that the sulphidic form of the catalyst is preserved.

In the preparation of technical white oils of a hydrocarbon mixture via a treatment with hydrogen according to the invention very favourable results can be obtained, if one of the following catalysts is applied.

(a) A catalyst prepared by a process which includes the steps of impregnating alumina with a solution containing one or more nickel and/or cobalt compounds, one or more molybdenum and/or tungsten compounds, phosphate ions and peroxide, followed by drying and calcination of the composition.

(b) A catalyst prepared by a process which includes the steps of incorporating in an alumina hydrogel one or more nickel and/or cobalt compounds and one or more molybdenum and/or tungsten compounds in concentrations which suffice to give the prepared catalyst a metal content, expressed in terms of metal oxides, of from 30 to 65%w, followed by drying and calcination of the composition; the alumina hydrogel in which the metal compounds are incorporated being a hydrogel which, upon drying and calcination, produces a xerogel with a bulk density of from 0.75 to 1.6 g/ml and a pore volume of from 0.15 to 0.5 ml/g.

(c) A catalyst prepared by a process which includes the steps of treating a composition containing alumina, water and one or more water-soluble salts of nickel and/or cobalt and one or more water-soluble salts of molybdenum and/or tungsten with a gas containing hydrogen sulphide at a temperature lower than 150° C and subsequently by heating the material in a hydrogen atmosphere to a final temperature higher than 200° C; the quantity of water present in the composition which is treated with the gas containing hydrogen sulphide corresponding to the quantity of water present in the composition after drying in a dry

gas at 110° C, increased by 20 to 120% of the quantity of water that the pores of the carrier of the dried composition can take up at 20° C.

The catalytically active metal components of the catalysts that are applied in the process according to the invention are preferred to be nickel and molybdenum or nickel and tungsten.

The hydrocarbon mixture which is applied in the process according to the invention as feed for the preparation of technical white oils can for instance be a mineral oil distillate obtained in the distillation of crude mineral oil at atmospheric or reduced pressure. Hydrocarbon mixtures obtained as raffinate in the treatment of a mineral oil distillate with a selective solvent for aromatic hydrocarbons, such as furfural, sulphur dioxide, phenol, cresol or chlorex are very suitable feeds for the preparation of technical white oils according to the invention. The feed which is applied in the process according to the invention preferably contains less than 40%w of aromatics. The initial boiling point of feed preferably lies above 200° C. If the hydrocarbon mixture used as the starting material in the process according to the invention has a high paraffin content, whereas a technical white oil with a low pour point has to be prepared, a dewaxing procedure has to be carried out. The starting material can be dewaxed or, alternatively, the technical white oil prepared from it. Dewaxing can be carried out by cooling the oil in the presence of a solvent. Very suitable for this purpose are a mixture of methyl ethyl ketone and toluene, a temperature between -10° and -40° C and a solvent to oil volume ratio between 1:1 and 10:1.

Suitable conditions for carrying out the catalytic treatment with hydrogen according to the invention are a hydrogen partial pressure of 25—200 bar, a space velocity of 0.1—5 and in particular of 0.5—2 kg.l⁻¹.h⁻¹, and a hydrogen/feed ratio of 50—5000 Ni H₂/kg feed. Depending on the viscosity of the starting material, the catalytic treatment with hydrogen according to the invention is preferably carried out under the following conditions. If the kinematic viscosity of the starting material at 100° F amounts to at most 25 cSt, the catalytic treatment with hydrogen is preferably carried out at a temperature of 275—350° C and a hydrogen partial pressure of 25—125 bar. If the kinematic viscosity of the starting material at 100° F amounts to more than 25 cSt, the catalytic treatment with hydrogen is preferably carried out at a temperature of 325—375° C and a hydrogen partial pressure of 75—200 bar.

Apart from being applied for the preparation of technical white oils, the process according to the invention can also very suitably serve as the first stage of a two-stage process for the preparation of medicinal oils by

catalytic treatment with hydrogen of a hydrocarbon mixture, using a noble metal catalyst in the second stage.

The invention is now elucidated with the aid of the following examples.

Nine catalysts (I—IX) were applied in the preparation of technical white oils via a treatment with hydrogen of two feeds (A and B). The catalysts and feeds are further specified below.

Catalysts I—III:

Ni/Mo/P/Al₂O₃ catalysts containing 4.2 parts by weight of nickel, 17.7 parts by weight of molybdenum and 3.1 parts by weight of phosphorus per 100 parts by weight of alumina. Catalysts I and II contained in addition 2.0 parts by weight of fluorine per 100 parts by weight of alumina. Catalyst III did not contain fluorine. These catalysts had been prepared by co-impregnation of alumina with an aqueous solution containing nickel nitrate, phosphoric acid, ammonium molybdate and hydrogen peroxide, followed by drying and calcination of the composition.

Catalysts IV—VI:

Ni/W/Al₂O₃ catalysts containing 15 parts by weight of nickel and 39 parts by weight of tungsten per 100 parts by weight of alumina. Catalysts IV and V contained in addition 8 parts by weight of fluorine per 100 parts by weight of alumina. Catalyst VI did not contain fluorine. These catalysts had been prepared by mixing an alumina hydrogel with an aqueous solution containing nickel nitrate and ammonium tungstate, of which solution the pH had been adjusted to 6.5 with the aid of 25% of ammonia. The mixture was heated to 80° C; the gel was filtered, extruded, dried and calcined. The alumina hydrogel which was used in the preparation of these catalysts, upon drying and calcination, produced a xerogel with a bulk density between 0.75 and 1.6 g/ml and a pore volume between 0.15 and 0.5 ml/g.

Catalysts VII—IX:

Ni/W/Al₂O₃ catalysts containing 6.6 parts by weight of nickel and 50.8 parts by weight of tungsten per 100 parts by weight of alumina. Catalysts VII and VIII contained in addition 2.0 parts by weight of fluorine per 100 parts by weight of alumina. Catalyst IX did not contain fluorine. These catalysts had been prepared by co-impregnation of alumina with an aqueous solution of nickel nitrate and ammonium tungstate. After adjusting the degree of wetting at 100%, the composition was first treated for 16 hours with H₂S at 15 bar and 75° C; then heated up to 400° C in two hours in a H₂S-containing stream of H₂ (9% v H₂S, 10 bar, 25,000 NL.1⁻¹.h⁻¹) and finally held in this gas stream for about two hours. The expression "degree of wetting" used in the foregoing refers to the quantity of water

present in the composition in addition to the quantity of water present therein after the composition has been dried in a dry gas at 110° C. The degree of wetting is expressed as a percentage of the quantity of water the pores of the carrier of the dried composition can take up at 20° C.

In the fluorine-containing catalysts I, IV and VII fluorine had been incorporated by in-situ fluorination, carried out by adding ortho-fluorotoluene to the feed during the initial stage of the treatment with hydrogen. In the fluorine-containing catalysts II, V and VIII fluorine had been incorporated by impregnation, carried out by adding ammonium fluoride to the aqueous metal salt-containing solution which was applied in the preparation of the catalysts.

Feed A

Raffinate obtained by extraction of a mineral oil distillate with sulphur dioxide. The mineral oil distillate was a neutral distillate obtained by the distillation at reduced pressure of a naphthenic crude oil. The raffinate had the following properties.

Kinematic viscosity at 100° F: 15.2 cSt
Sulphur content: 0.23% w
Aromatics content: 12% w
Colour (ASTM D 1500): L 1.0

Feed B

Raffinate obtained by extraction of a mineral oil distillate with furfural. The mineral oil distillate was a neutral distillate obtained by the distillation at reduced pressure of a naphthenic crude oil. The raffinate had the following properties.

Kinematic viscosity at 100° F: 138 cSt
Sulphur content: 0.88% w
Aromatics content: 34% w
Colour (ASTM D 1500): 2.0

The catalysts were applied in the sulphidic form. The catalysts I—VI were sulphided by contacting them with hydrogen and a sulphur-containing gas oil. From the liquid products obtained from the treatment with hydrogen light components were removed by distillation. From the liquid products obtained from feed A products were isolated with an initial boiling point of 290° C and from those obtained from feed B products with an initial boiling point of 310° C. The conditions under which the treatments with hydrogen were carried out as well as the properties of the 290° C⁺ and the 310° C⁺ products are listed in the table. In all experiments the starting material was converted into a liquid product consisting to an extent of less than 30% w of components with a boiling point lower than the initial boiling point of the feed. All the products prepared were almost tasteless and odourless.

TABLE

Exp. No.	Feed No.	Cat. No.	Process conditions				Yield of 290°C ⁺ and 310°C ⁺ product, respectively, %w	Product properties			
			temp., °C.	hydrogen partial pressure bar	space velocity, kg.l ⁻¹ .h ⁻¹	hydrogen/ feed ratio NL/kg		kinematic viscosity at 100°F, cSt	aromatics content mmols/ 100 g	Saybolt colour	result of FDA test No. 121,2589
1	A	I	325	150	0.75	300	89	13.5	2.1	>+30	+
2	A	I	310	150	0.75	300	97	13.9	2.8	>+30	+
3	A	II	325	150	0.75	150	95	14.0	6.5	+12	-
4	A	II	325	150	0.5	300	87	13.5	5.2	+22	-
5	A	III	350	100	0.5	150	86	13.3	9.6	+6	-
6	A	III	325	150	0.5	150	94	15.7	7.2	+17	-
7	A	IV	295	150	0.75	300	98	14.3	2.8	>+30	+
8	A	IV	325	150	0.75	300	96	13.6	1.0	>+30	+
9	A	IV	310	100	0.5	300	97	14.0	1.1	>+30	+
10	A	IV	325	150	2.0	300	98	14.3	2.9	>+30	+
11	A	V	295	150	0.75	300	98	14.4	3.5	>+26	-
12	A	V	310	100	0.5	300	97	14.2	4.5	+28	-
13	A	VI	295	150	0.75	300	98	14.3	6.2	+19	-
14	B	IV	340	150	0.75	300	93	79.1	12.7	>+30	+
15	B	IV	330	100	0.5	300	94	89.4	28.2	>+30	+
16	B	V	340	150	0.75	300	94	82.0	26.2	+22	-

TABLE (continued)

Exp. No.	Feed No.	Cat. No.	Process conditions				Yield of 290°C ⁺ and 310°C ⁺ product, respectively, %w	Product properties			
			temp., °C	hydrogen partial pressure, bar	space velocity, kg.l ⁻¹ .h ⁻¹	hydrogen feed ratio, NI/kg		kinematic viscosity at 100°F, cSt	aromatics content, mmols/100 g	Saybolt colour	result of FDA test No. 121,2589
17	B	V	330	100	0.5	300	95	95.0	41.7	+15	-
18	B	VI	340	150	0.75	300	95	87.9	33.0	+15	-
19	B	VI	330	100	0.5	300	96	101.4	54.6	+3	-
20	B	VII	350	150	0.75	300	87	75.3	19.1	>+30	+
21	B	VIII	350	150	0.75	300	89	77.9	28.8	+25	-
22	B	IX	350	150	0.75	300	94	86.7	37.8	-3	-

Experiments 1,2,7—10, 14,15 and 20 refer to treatments with hydrogen according to the invention. In these experiments catalysts fluorinated in-situ were applied (I, IV and VII) and oils were obtained which completely met the specifications formulated in this patent application for technical white oils. In addition, it was found that the oils prepared according to experiments 2,7 and 9 also met the specifications according to F.D.A. No. 121,1146.

Experiments 3—6, 11—13, 16—19, 21 and 22 refer to treatments with hydrogen outside the scope of the invention. In these experiments fluorine-containing catalysts were applied in which fluorine had been incorporated by impregnation (II, V and VIII) as

well as fluorine-free catalysts (III, VI and IX), and oils were obtained which, as far as their colour and performance in F.D.A. test No. 121,2589 were concerned, did not meet the specifications formulated in this patent application for technical white oils.

WHAT WE CLAIM IS:—

1. A process for the preparation of technical white oils, characterized in that a hydrocarbon mixture is converted into a liquid product, consisting to an extent of less than 30% by weight of components with a boiling point lower than the initial boiling point of the feed, by a treatment with hydrogen at a temperature between 275 and 375° C in the presence of a fluorine-containing sulphidic catalyst

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TABLE (continued)

Exp. No.	Feed No.	Cat. No.	Process conditions				Yield of 290°C ⁺ and 310°C ⁺ product, respectively, %w	Product properties			
			temp., °C	hydrogen partial pressure bar	space velocity kg.l ⁻¹ .h ⁻¹	hydrogen/feed ratio NI/kg		kinematic viscosity at 100°F cSt	aromatics content mmols/ 100 g	Saybolt colour	result of FDA test No. 121,2589
17	B	V	330	100	0.5	300	95	95.0	41.7	+15	-
18	B	VI	340	150	0.75	300	95	87.9	33.0	+15	-
19	B	VI	330	100	0.5	300	96	101.4	54.6	+ 3	-
20	B	VII	350	150	0.75	300	87	75.3	19.1	>+30	+
21	B	VIII	350	150	0.75	300	89	77.9	28.8	+25	-
22	B	IX	350	150	0.75	300	94	86.7	37.8	- 3	-

Experiments 1,2,7—10, 14,15 and 20 refer to treatments with hydrogen according to the invention. In these experiments catalysts fluorinated in-situ were applied (I, IV and VII) and oils were obtained which completely met the specifications formulated in this patent application for technical white oils. In addition, it was found that the oils prepared according to experiments 2,7 and 9 also met the specifications according to F.D.A. No. 121,1146.

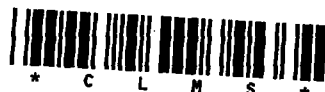
Experiments 3—6, 11—13, 16—19, 21 and 22 refer to treatments with hydrogen outside the scope of the invention. In these experiments fluorine-containing catalysts were applied in which fluorine had been incorporated by impregnation (II, V and VIII) as

well as fluorine-free catalysts (III, VI and IX), and oils were obtained which, as far as their colour and performance in F.D.A. test No. 121,2589 were concerned, did not meet the specifications formulated in this patent application for technical white oils.

WHAT WE CLAIM IS:—

1. A process for the preparation of technical white oils, characterized in that a hydrocarbon mixture is converted into a liquid product, consisting to an extent of less than 30% by weight of components with a boiling point lower than the initial boiling point of the feed, by a treatment with hydrogen at a temperature between 275 and 375° C in the presence of a fluorine-containing sulphidic catalyst





- comprising nickel and/or cobalt and, in addition, molybdenum and/or tungsten on a carrier and in which at least part of the fluorine has been incorporated by in-situ fluorination, and that from the product obtained in the treatment with hydrogen the desired technical white oil is isolated by topping off light components. 70
2. A process according to claim 1, characterized in that more than 50% of the fluorine and preferably almost all of the fluorine present in the catalyst has been incorporated therein by in-situ fluorination. 75
3. A process according to claim 1 or 2, characterized in that the in-situ fluorination of the catalyst has been carried out by continuously adding a quantity of 20—5,000 ppmw and preferably 30—2,000 ppmw of fluorine, in the form of a fluorine compound, to the gas and/or liquid stream which is passed over the catalyst until the required quantity of fluorine has been incorporated in the catalyst. 80
4. A process according to any one of claims 1—3, characterized in that the in-situ fluorination of the catalyst is carried out at an early stage of the treatment with hydrogen. 85
5. A process according to any one of claims 1—4, characterized in that during the treatment with hydrogen, after the required quantity of fluorine has been incorporated in the catalyst by in-situ fluorination, a quantity of 1—50 ppmw and preferably 5—25 ppmw of fluorine, in the form of a fluorine compound, is continuously added to the gas and/or liquid stream that is passed over the catalyst. 90
6. A process according to any one of claims 1—5, characterized in that the catalyst contains 0.5—25 parts by weight and preferably 1—10 parts by weight of fluorine per 100 parts by weight of carrier. 95
7. A process according to any one of claims 1—6, characterized in that the catalyst contains 1—30 parts by weight and preferably 2—20 parts by weight of nickel and/or cobalt and, in addition, 1—80 parts by weight and preferably 10—80 parts by weight of molybdenum and/or tungsten per 100 parts by weight of carrier. 100
8. A process according to any one of claims 1—7, characterized in that a catalyst is applied of which the weight ratio of nickel and/or cobalt on the one hand to molybdenum and/or tungsten on the other, lies between 1:1 and 1:10. 105
9. A process according to any one of claims 1—8, characterized in that the catalyst contains alumina as a carrier. 110
10. A process according to any one of claims 1—9, characterized in that the catalyst has a surface area of 50—500 m²/g and a pore volume of 0.2—1.0 ml/g. 115
11. A process according to any one of claims 1—10, characterized in that the catalyst applied has been prepared by a process which includes the steps of impregnating alumina with a solution containing one or more nickel and/or cobalt compounds, one or more molybdenum and/or tungsten compounds, phosphate ions and peroxide ions, followed by drying and calcination of the composition. 120
12. A process according to any one of claims 1—10, characterized in that the catalyst applied has been prepared by a process which includes the steps of incorporating in an alumina hydrogel one or more nickel and/or cobalt compounds and one or more molybdenum and/or tungsten compounds in a concentration which suffices to give the prepared catalyst a metal content, expressed in metal oxides, of from 30 to 65% by weight, followed by drying and calcination of the composition; the alumina hydrogel in which the metal compounds are incorporated being a hydrogel which, upon drying and calcination, yields a xerogel with a bulk density of from 0.75 to 1.6 g/ml and a pore volume of from 0.15 to 0.5 ml/g. 125
13. A process according to any one of claims 1—10, characterized in that the catalyst applied has been prepared by a process which includes the steps of treating a composition containing alumina, water, one or more water-soluble salts of nickel and/or cobalt and one or more water-soluble salts of molybdenum and/or tungsten, with a gas containing hydrogen sulphide at a temperature lower than 150° C and subsequently heating the material in a hydrogen atmosphere to a final temperature higher than 200° C; the quantity of water present in the composition which is treated with the gas containing hydrogen sulphide corresponding to the quantity of water present in the composition after drying in a dry gas at 110° C, increased by 20 to 120% of the quantity of water that the pores of the carrier of the dried composition can take up at 20° C. 130
14. A process according to any one of claims 1—13, characterized in that the catalyst contains as catalytically active metal components nickel and molybdenum or nickel and tungsten. 135
15. A process according to any one of claims 1—14, characterized in that the hydrocarbon mixture which is used as the starting material in the process, is a mineral oil distillate obtained in the distillation of a crude mineral oil at atmospheric or reduced pressure. 140
16. A process according to any one of claims 1—14, characterized in that the hydrocarbon mixture which is used as the starting material in the process is a raffinate obtained in the treatment of a mineral oil distillate with a selective solvent for aromatic hydrocarbons. 145
17. A process according to any one of claims 1—16, characterized in that the hydrocarbon mixture which is used as the start-



ing material in the process has an aromatics content lower than 40% by weight and an initial boiling point higher than 200° C.

- 5 18. A process according to any one of claims 1—17, characterized in that the catalytic treatment with hydrogen is carried out at a hydrogen partial pressure of 25—200 bar, a space velocity of 0.1—5 and preferably 0.5—2 kg.l⁻¹.h⁻¹ and a hydrogen/feed ratio of 50—5,000 Nl H₂/kg feed.

- 10 19. A process according to any one of claims 1—18, characterized in that the hydrocarbon mixture which is used as the starting material in the process has a kinematic viscosity at 100° F of at most 25 cS and that the catalytic treatment with hydrogen is carried out at a temperature of 275—350° C and a hydrogen partial pressure of 25—125 bar.

- 20 20. A process according to any one of claims 1—18, characterized in that the hydrocarbon mixture which is used as the starting material in the process has a kinematic viscosity at 100° F of more than 25 cS and that the catalytic treatment with hydrogen is carried out at a temperature of 325—375° C and a hydrogen partial pressure of 75—200 bar.

21. A process according to any one of claims 1—20, characterized in that a technical white oil is prepared which meets the specifications according to F.D.A. No. 121,1146. 30

22. A process as claimed in claim 1 and substantially as hereinbefore described with reference to any one of Experiments 1,2,7— 10,14,15 and 20. 35

23. Technical white oils prepared by the process according to any one of claims 1—22.

24. A process according to any one of claims 1—22, characterized in that the technical white oil obtained is processed into a medicinal oil by catalytic treatment with hydrogen using a noble metal catalyst. 40

25. A process as claimed in claim 24 and substantially as hereinbefore described with reference to any one of Experiments 2,7 and 9. 45

26. Medicinal oils prepared by the process claimed in claim 24 or claim 25.

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