

PATENT SPECIFICATION

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(54) PROCESS FOR THE PREPARATION OF MEDICINAL OILS

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present patent application relates to a process for the preparation of medicinal oils. In this patent application the term medicinal oils is used to designate hydrocarbon oils without smell and taste, having a colour Saybolt higher than +30 and complying with the "hot acid" test according to ASTM—D 565 and the requirements as specified in FDA No. 121.1146. In the "hot acid" test according to ASTM—D 565 the oil is treated with concentrated sulphuric acid. Both substances are heated and mixed. As a result, two layers are formed: an oil and an acid layer. The colours of the two layers are inspected. To conform to this test the oil layer must not discolour at all. The acid layer may change colour only slightly. It must not become darker than a given reference solution. The requirement as specified in FDA No. 121.1146 involves that the UV absorption of the oil in the wavelength region of 260—350 nm is at most 0.10.

Medicinal oils are, among other uses, applied on a large scale in the plastic, cosmetic, food and pharmaceutical industries. One of their modes of preparation is to treat a hydrocarbon mixture with a suitable viscosity with a large quantity of concentrated sulphuric acid, neutralize it and subject it to a clay treatment. This process involves a number of drawbacks. The main drawback relates to the waste products, consisting of acid tar and spent clay, obtained in the process. In connection with the tightening up of the legislation concerning environmental hygiene the disposal of these waste products, which are

obtained in the process in considerable quantities, constitutes an increasingly serious problem. Another drawback of the aforementioned process relates to the yield. Dependent on the quantity of undesired components present in the starting material and removed in the various refining steps, the process may give a relatively low yield of medicinal oil. Finally, the process is fairly costly.

To circumvent the afore-mentioned drawbacks in the preparation of medicinal oils it has already been suggested that these oils be prepared via a catalytic hydrogen treatment. For this purpose a hydrocarbon mixture with a suitable viscosity is contacted with a catalyst at elevated temperature and pressure and in the presence of hydrogen. As this process obviates the use of a large quantity of concentrated sulphuric acid and hence also the formation of a considerable quantity of acid tar, the problem of waste products in this process is insignificant. Since, in addition, undesired components present in the starting material are in this process converted into valuable medicinal oil components instead of being removed therefrom, this process leads to a considerably higher yield than the aforementioned process via treatment with a large quantity of concentrated sulphuric acid. Finally, the process is much less costly.

When medicinal oils are prepared via a catalytic hydrogen treatment the activity of the catalyst plays a very important role. According as the catalyst has a lower activity, the temperature applied should be higher in order to achieve the desired conversion. Higher temperatures promote cracking reactions, as a result of which the yield of medicinal oil drops and the hydrogen consumption rises. Besides, higher temperatures promote the formation of structures which have an adverse effect on the results of the test according to FDA No. 121.1146 and the "hot acid" test according to ASTM—D 565. In a number of cases it appears therefore that medicinal

oils prepared via a catalytic hydrogen treatment do not yet fully conform to the requirements for medicinal oils specified in this patent application, so that an additional light acid and/or clay treatment has to be applied to bring these oils to specification. It has now been found that medicinal oils fully conforming to the requirements specified in this patent application without an additional acid and/or clay treatment being necessary, can be prepared in a high yield via a catalytic hydrogen treatment by starting from a hydrocarbon mixture with an aromatics content below 10 %w and using a catalyst containing one or more noble metals from Group VIII on a carrier, which carrier contains 13—15 %w of alumina, the remainder being silica. It has also been found that the oils prepared in this way comply in a number of cases, not only with the requirement specified in this patent application, but also even with those of UV absorption as incorporated in the British and/or German Pharmacopoeias. According to the British Pharmacopoeia the UV absorption of the oil in the wavelength region of 240—280 nm should be at most 0.10. According to the German Pharmacopoeia (DAB 7) the UV absorption of the oil at a wavelength of 275 nm, 295 nm and 300 nm and higher, should be at most 0.80, 0.04 and 0.30, respectively.

The present patent application therefore relates to a process for the preparation of medicinal oils, in which a hydrocarbon mixture with an aromatics content of less than 10 %w is contacted at elevated temperature and pressure and in the presence of hydrogen with a catalyst containing one or more noble metals from Group VIII on a carrier, which carrier contains 13—15 %w of alumina, the remainder being silica.

The present catalysts whose carrier comprises 13—15 %w of alumina, the remainder being silica, show an appreciably better suitability for the preparation of medicinal oils via a hydrogen treatment than catalysts with the same metal load whose carrier consists exclusively of alumina or exclusively of silica. That this better suitability must at least partly be ascribed to the specific alumina content of the carrier appears from the fact that the present catalysts, whose carrier comprises 13—15 %w of alumina, the remainder being silica, also show a considerably better suitability for the preparation of medicinal oils via a hydrogen treatment than catalysts with the same metal load on a silica-alumina carrier, but which carrier has a higher or lower alumina content.

The catalysts applied in the process according to the invention contain one or more noble metals from Group VIII on a silica-alumina carrier. The quantity of noble metal from Group VIII present on the carrier may vary within wide limits, but is frequently 0.05—5

%w. The noble metals from Group VIII which may be present on the carrier are platinum, palladium, rhodium, ruthenium, iridium and osmium, platinum being preferred. If desired, two or more of these metals may be present in the catalysts. The quantity of noble metal from Group VIII which is present in the catalyst is preferably 0.1—2 %w and in particular 0.2—1 %w. In addition, catalysts with a surface area of 50—500 m²/g and a pore volume of 0.2—1.2 ml/g are preferred.

The catalysts applied in the process according to the invention may be prepared according to any process known in the art for the preparation of catalysts containing one or more noble metals on a carrier. The catalysts are preferably prepared by impregnating a silica-alumina carrier with an aqueous solution containing one or more noble metal compounds, the composition thus obtained being dried and calcined. Suitable silica-alumina carriers may, for example, be prepared by precipitating silica and alumina simultaneously or by impregnating a silica with an aluminium compound and subsequently drying and calcining the material. The silica-aluminas applied as carriers for the catalysts according to the invention are preferably prepared by precipitating alumina or a silica hydrogel and subsequently drying and calcining the material. This preparation is preferably carried out by starting from an aqueous silicate solution (for example water glass), lowering its pH as a result of which a silica hydrogel precipitates, allowing the silica hydrogel to age, adding an aqueous solution of an aluminium compound, increasing the pH as a result of which alumina precipitates on the silica hydrogel, drying and calcining. Ageing of the silica hydrogel may suitably be carried out by storing the gel for 4—200 hours at a pH of between 7 and 11 at elevated temperature. During ageing the pore volume of the silica hydrogel increases and the surface area decreases, the result being that the material becomes more suitable for catalytic purposes.

If desired, the catalysts applied in the process according to the invention may contain a halogen, for example fluorine.

As hydrocarbon mixtures with an aromatics content of lower than 10 %w applicable as feeds for the preparation of medicinal oils according to the invention are eligible, for example, mineral oil distillates obtained in the distillation of crude mineral oil at atmospheric or reduced pressure, as well as raffinates obtained in treating mineral oil distillates with a selective solvent for aromatic hydrocarbons, such as furfural, sulphur dioxide, phenol, cresol or chlorex. The feed used in the process according to the invention contains preferably less than 25 wppm of sulphur. If the hydrocarbon mixture used as starting material in the process according to the invention has

a high paraffin wax content, whilst a medicinal oil with a low pour point has to be prepared, dewaxing is necessary. This dewaxing can be applied either to the starting material or to the medicinal oil prepared therefrom. Dewaxing can be carried out by cooling the oil in the presence of a solvent. 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 are very suitable for this purpose.

Suitable conditions for carrying out the catalytic hydrogen treatment according to the invention are a temperature of 200 – 300°C ., a hydrogen partial pressure of 25 – 200 bar, a space velocity of 0.1 – 5 and in particular of 0.5 – $2\text{ kg.l}^{-1}\text{.h}^{-1}$ and a hydrogen/feed ratio of 50 – $5000\text{ NI H}_2/\text{kg feed}$. Dependent on the viscosity of the starting material the catalytic hydrogen treatment according to the invention is preferably carried out under the following conditions. If the kinematic viscosity of the starting material at 100°F . is at most 25 cS , the catalytic hydrogen treatment is preferably carried out at a temperature of 200 – 260°C . and a hydrogen partial pressure of 25 – 150 bar. If the kinematic viscosity of the starting material at 100°F . is more than 25 cS , the catalytic hydrogen treatment is preferably carried out at a temperature of 240 – 300°C . and a hydrogen partial pressure of 100 – 200 bar.

The process according to the invention is particularly of importance for application as second step of a two-step process for the preparation of medicinal oils by catalytic hydrogen treatment of a hydrocarbon mixture, using a sulphidic catalyst containing nickel and/or cobalt and in addition molybdenum and/or tungsten on a carrier in the first step. The catalyst applied in the first step of this two-step process contains preferably 1 – 30 parts by weight and in particular 2 – 20 parts by weight of nickel and/or cobalt and in addition 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 ratio by weight between nickel and/or cobalt on the one hand and molybdenum and/or tungsten on the other is preferably between $1:1$ and $10:1$. The carrier used for the sulphidic catalyst is preferably alumina.

Very suitable catalysts for carrying out the first step of the above two-step process are:

- (a) A catalyst prepared by 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 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 sufficient to impart to the ready catalyst a metal content, expressed as metal oxides, of 30 to $65\text{ \%w}$, followed by drying and calcination of the composition; the alumina hydrogel in which the metal compounds are incorporated should be a hydrogel which after drying and calcination yields a xerogel with a bulk density of 0.75 to 1.6 g/ml and a pore volume of 0.15 to 0.5 ml/g .

- (c) a catalyst prepared by 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 hydrogen-sulphide-containing gas at a temperature of below 150°C . and subsequently heating the material in a hydrogen-containing gas to a final temperature of above 200°C .; the quantity of water present in the composition treated with the hydrogen-sulphide-containing gas should correspond with 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 which the dried composition can take up in the pores of the carrier at 20°C .

In addition to the metals nickel and/or cobalt and molybdenum and/or tungsten the sulphidic catalysts used in the first step of the afore-mentioned two-step process preferably contain fluorine. The incorporation of fluorine in the catalysts can in principle be effected in two ways. Fluorine can be incorporated in the catalyst by impregnating the latter during or after its preparation with a suitable fluorine compound such as ammonium fluoride. It is also possible to incorporate the fluorine in the catalyst by in-situ fluorination of the catalyst in an early stage of the hydrogen treatment for which the catalyst is used (for example during or after starting the process). In-situ fluorination of the catalyst can be carried out by adding a suitable fluorine compound, such as ortho-fluorotoluene or difluoroethane to the gas and/or liquid stream which is passed over the catalyst. Preferred are sulphidic catalysts in which more than 50% of the fluorine and in particular virtually all the fluorine has been incorporated by fluorination in situ. The sulphidic catalysts contain preferably 0.5 – 25 parts by weight and in particular 1 – 10 parts by weight of fluorine per 100 parts by weight of carrier.

The hydrocarbon mixture applied in the aforementioned two-step process for the preparation of medicinal oils as feed for the first

step may, for example, be a mineral oil distillate obtained in the distillation of crude mineral oil at atmospheric or reduced pressure. Very suitable as feed for the first step of the afore-mentioned two-step process for the preparation of medicinal oils are hydrocarbon mixtures obtained as raffinate in treating a mineral oil distillate with a selective solvent for aromatic hydrocarbons. The feed for the first step of the two-step process contains preferably less than 40 %w of aromatics and has preferably an initial boiling point of 200° C.

Suitable conditions for carrying out the first step of the two-step process for the preparation of medicinal oils are a temperature of 275—375° C., a hydrogen partial pressure of 25—200 bar, a space velocity of 0.1—5, in particular 0.5—2 kg.l⁻¹.h⁻¹ and a hydrogen/feed ratio of 50—500 NI H₂/kg feed. Dependent on the viscosity of the starting material the first step of the two-step process is preferably carried out under the following conditions. If the kinematic viscosity of the starting material at 100° F. is at most 25 cS, the first step 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. is more than 25 cS, the first step is preferably carried out at a temperature of 325—375° C. and a hydrogen partial pressure of 75—200 bar.

The first step of the two-step process is preferably carried out such that a liquid product is obtained less than 30 %w of which consists of components with a boiling point below the initial boiling point of the feed.

The invention will now be described with reference to the following experiments:

Six noble metal catalysts (I—VI) were applied for the preparation of medicinal oils via a hydrogen treatment of three feeds (A—C). The feeds A—C had been prepared by hydrogen treatment of two feeds (a and b) using two sulphidic catalysts (1 and 2). The catalysts and feeds will be further described hereinafter.

Feed a

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

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

Feed b

Raffinate obtained in the extraction of a mineral oil distillate with furfural. The min-

eral oil distillate was a neutral distillate obtained in the distillation at reduced pressure of a naphthenic crude oil. The raffinate had the following properties:

Kinematic viscosity at 100° F.: 138 cS
Sulphur content: 0.88 %w
Aromatics content: 34 %w
Colour (ASTM—D1500): 2.0.

Catalyst 1

Ni/Mo/P/F/Al₂O₃ catalyst containing 4.2 parts by weight of nickel, 17.7 parts by weight of molybdenum, 3.1 parts by weight of phosphorus and 2.0 parts by weight of fluorine per 100 parts by weight of alumina. This catalyst 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.

Catalyst 2

Ni/W/F/Al₂O₃ catalyst containing 15 parts by weight of nickel, 39 parts by weight of tungsten and 8 parts by weight of fluorine per 100 parts by weight of alumina. This catalyst had been prepared by mixing an alumina hydrogel with an aqueous solution containing nickel nitrate and ammonium tungstate, the pH of which solution had by means of 25% of ammonia been brought to 6.5. The mixture was heated to 80° C.; the gel was filtered, extruded, dried and calcined. The alumina hydrogel used in the preparation of this catalyst yielded after drying and calcination a xerogel with a bulk density of between 0.75 and 1.6 g/ml and a pore volume of between 0.15 and 0.5 ml/g.

Fluorine was incorporated in catalysts 1 and 2 by fluorination in situ by adding ortho-fluorotoluene to the feed during the initial phase of the hydrogen treatment in which the catalyst was applied. Catalysts 1 and 2 were applied in sulphidic form. Sulphidation was performed by bringing the catalysts into contact with hydrogen and a sulphur-containing gas oil.

FEED A

Feed A was prepared by catalytic hydrogen treatment of feed a in the presence of catalyst 1 and under the following conditions:

temperature: 320° C.
hydrogen partial pressure: 150 bar
space velocity: 0.75 kg.l⁻¹.h⁻¹
hydrogen/feed ratio: 300 NI H₂/kg feed.

Feed A (liquid reaction product) contained 0.7 %w of aromatics and 5 wppm of sulphur. By distilling off light components from feed A a product could be obtained with an initial boiling point of 290° C., in a yield of 89 %w

on feed a. This product had the following properties:

kinematic viscosity at 100° F.: 14.0 cS
aromatics content: 1.4 mmol/100 g
colour Saybolt: +20.

FEED B

Feed B was prepared by catalytic hydrogen treatment of feed b in the presence of catalyst 1 and under the following conditions:

temperature: 360° C.
hydrogen partial pressure: 150 bar
space velocity: 0.75 kg.l⁻¹.h⁻¹
hydrogen/feed ratio: 300 NI H₂/kg feed.

Feed B (liquid reaction product) contained 5.2 %w of aromatics and 4 wppm of sulphur. By distilling off light components from feed B a product could be obtained with an initial boiling point of 310° C., in a yield of 78 %w calculated on feed b. This product had the following properties:

kinematic viscosity at 100° F.: 47.1 cS
aromatics content: 11.7 mmol/100 g
colour Saybolt: +17.

FEED C

Feed C was prepared by catalytic hydrogen treatment of feed b in the presence of catalyst 2 and under the following conditions:

temperature: 350° C.
hydrogen partial pressure: 150 bar
space velocity: 0.75 kg.l⁻¹.h⁻¹
hydrogen/feed ratio: 300 NI H₂/kg feed.

Feed C (liquid reaction product) contained 4.5 %w of aromatics and 4 wppm of sulphur. By distilling off light components from feed C a product could be obtained with an initial boiling point of 310° C. and a yield of 90 %w calculated on feed b. This product had the following properties:

kinematic viscosity at 100° F.: 77 cS
aromatics content: 8.0 mmol/100g
colour Saybolt: +29.

Feeds A, B and C comprised less than 30 %w of components with a boiling point below the initial boiling point of feed a and b, respectively, from which they had been prepared.

CATALYST I

Pt/SiO₂/—Al₂O₃ catalyst with a surface area of 450 m²/g and a pore volume of 0.47 ml/g. Platinum content: 0.87 %w. The silica-alumina carrier consisted of 14.6 %w of alumina and 85.4 %w of silica and had a

surface area of 505 m²/g and a pore volume of 0.56 ml/g.

CATALYST II

Pt/SiO₂—Al₂O₃ catalyst with a surface area of 342 m²/g and a pore volume of 0.78 ml/g. Platinum content: 0.87 %w. The silica-alumina carrier consisted of 13.2 %w of alumina and 86.8 %w of silica and had a surface area of 388 m²/g and a pore volume of 0.87 ml/g.

CATALYST III

Pt/SiO₂—Al₂O₃ catalyst with a platinum content of 0.87 %w. The silica-alumina carrier consisted of 17.0 %w of alumina and 83.0 %w of silica and had a surface area of 518 m²/g and a pore volume of 0.49 ml/g.

CATALYST IV

Pt/SiO₂—Al₂O₃ catalyst with a platinum content of 0.87 %w. The silica-alumina carrier consisted of 8.0 %w of alumina and 92.0 %w of silica and had a surface area of 110 m²/g and a pore volume of 0.34 ml/g.

CATALYST V

Pt/Al₂O₃ catalyst with a platinum content of 0.85 %w.

CATALYST VI

Pt/SiO₂ catalyst with a platinum content of 0.85 %w.

Catalysts I—VI were prepared by impregnating the relative carrier materials with an aqueous solution of H₂PtCl₆, followed by drying and calcination of the compositions.

From the liquid reaction products obtained in the hydrogen treatment of feeds A—C using catalysts I—VI, light components were removed by distillation. From the liquid reaction products obtained from feed A products were isolated with an initial boiling point of 290° C. and from those obtained from feeds B and C products with an initial boiling point of 310° C. The conditions under which the hydrogen treatments were carried out and the properties of the 290°C.+ and 310°C.+ are listed in the Table. The hydrogen/feed ratio was in all the hydrogen treatments 150 NI H₂/kg feed. All the products prepared were without taste and smell and contained less than 1 wppm of sulphur.

Experiments 1—6, 15—20, 29 and 30 relate to hydrogen treatments according to the invention. In these experiments silica-alumina-based platinum catalysts were used whose carrier had the correct alumina content (I and II) and oils were obtained which fully met the requirements specified for medicinal oils in this patent application. The oils prepared according to Experiments 1, 2, 15, 16 and 17 were in addition found to meet the UV

absorption requirements specified in the British Pharmacopoeia. Of these oils those prepared according to Experiments 1, 2 and 16 also met the UV absorption requirements specified in the German Pharmacopoeia.

Experiments 7—14, 21—28 and 31—34 relate to hydrogen treatments beyond the scope of the invention. In these experiments silica-alumina-based platinum catalysts were used whose carrier had either too high (III) or too

low (IV) an alumina content, as well as alumina (V) and silica (VI)-based platinum catalysts, oils being obtained which with respect to their behaviour in the "hot acid" test invariably failed the requirements specified for medicinal oils in this patent application and which as regards their colour and behaviour in the FDA test No. 121.1146 in most cases failed these requirements.

TABLE

Exp. No.	Feed No.	Cat. No.	Process conditions			Yield of 290°C ⁺ and 310°C ⁺ product, resp. %w	Product properties				
			temp., °C.	hydrogen partial pressure, bar	space velocity, kg.l ⁻¹ .h ⁻¹		kinematic viscosity at 100°F, cS	aromatics content, mmol/100 g	colour Saybolt	result "hot acid" test	result FDA test No. 121.1146
1	A	I	225	150	0.75	87	13.6	<0.1	>+30	+	+
2	A	I	250	150	0.75	86	13.4	0.1	>+30	+	+
3	A	I	225	150	1.5	88	13.8	0.1	>+30	+	+
4	A	I	250	100	0.75	85	13.1	0.1	>+30	+	+
5	A	II	250	150	0.75	85	13.2	0.1	>+30	+	+
6	A	II	250	100	0.5	84	13.0	0.1	>+30	+	+
7	A	III	225	150	0.75	86	13.7	0.3	27	-	-
8	A	III	250	150	0.75	85	13.6	0.3	25	-	-
9	A	IV	225	150	0.75	84	13.3	0.3	28	-	-
10	A	IV	250	150	0.75	84	12.9	0.4	21	-	-
11	A	V	225	150	0.75	88	13.9	0.4	29	-	+
12	A	V	250	150	0.75	88	13.9	0.4	28	-	+
13	A	VI	225	150	0.75	88	13.5	0.8	26	-	-
14	A	VI	250	150	0.75	88	13.4	1.0	22	-	-

TABLE (Continued)

Exp. No.	Feed No.	Cat. No.	Process conditions			Yield of 290°C ⁺ and 310°C ⁺ product, resp. %w	Product properties				result "hot acid" test	result FDA test No. 121.1146
			temp. °C.	hydrogen partial pressure, bar	space velocity kg.l ⁻¹ .h ⁻¹		kinematic viscosity at 100°F. cS	aromatics content, mmol/100 g	colour Saybolt			
15	B	I	250	150	0.75	76	44.9	0.3	>+30	+	+	
16	B	I	275	150	0.75	69	39.1	0.1	>+30	+	+	
17	B	I	250	100	0.5	77	45.4	0.5	>+30	+	+	
18	B	I	275	150	1.2	73	42.7	0.3	>+30	+	+	
19	B	II	250	150	0.75	77	45.2	0.4	>+30	+	+	
20	B	II	275	100	0.5	76	46.0	0.5	>+30	+	+	
21	B	III	250	150	0.75	77	46.0	0.9	27	-	-	
22	B	III	275	150	0.75	74	43.5	0.7	21	-	-	
23	B	IV	250	150	0.75	73	42.1	2.0	25	-	-	
24	B	IV	275	150	0.75	64	35.3	2.8	20	-	-	
25	B	V	250	150	0.75	77	45.3	1.1	29	-	+	
26	B	V	275	150	0.75	76	44.7	1.2	27	-	+	
27	B	VI	250	150	0.75	78	46.2	2.4	24	+	-	
28	B	VI	275	150	0.75	76	45.3	3.0	22	-	-	

TABLE (Continued)

Exp. No.	Feed No.	Cat. No.	Process conditions			Yield of 290°C ⁺ and 310°C ⁺ product, resp. %w	Product properties				
			temp., °C.	hydrogen partial pressure, bar	space velocity, kg.l ⁻¹ .h ⁻¹		kinematic viscosity, at 100°F, cS	aromatics content, mmol/100 g	colour Saybolt	result "hot acid" test	result FDA test No. 121.1146
29	C	I	250	150	0.75	85	75	0.1	>+30	+	+
30	C	I	250	150	2.0	87	76	0.3	>+30	+	+
31	C	III	250	150	0.75	88	76	0.6	>+30	-	-
32	C	IV	250	150	0.75	83	68	1.0	>+30	-	-
33	C	V	250	150	0.75	89	77	0.8	>+30	-	+
34	C	VI	250	150	0.75	89	76	2.0	+27	-	-

WHAT WE CLAIM IS:—

1. A process for the preparation of medicinal oils, characterized in that a hydrocarbon mixture with an aromatics content of less than 10 %w is contacted at elevated temperature and pressure and in the presence of hydrogen with a catalyst containing one or more noble metals from Group VIII on a carrier, which carrier contains 13—15 %w of alumina, the remainder being silica.

2. A process according to claim 1, characterized in that the catalyst contains 0.05—5 %w of noble metal.

3. A process according to claim 2, characterized in that the catalyst contains 0.1—2 %w and preferably 0.2—1 %w of noble metal.

4. A process according to any one of claims 1—3, characterized in that the catalyst contains platinum as noble metal.

5. A process according to any one of claims 1—4, characterized in that the catalyst has a surface area of 50—500 m²/g and a pore volume of 0.2—1.2 ml/g.

6. A process according to any one of claims 1—5, characterized in that the catalyst is prepared by impregnating a silica-alumina carrier with an aqueous solution containing

TABLE (Continued)

Exp. No.	Feed No.	Cat. No.	Process conditions			Yield of 290°C ⁺ and 310°C ⁺ product, resp. %w	Product properties				
			temp., °C.	hydrogen partial pressure, bar	space velocity, kg.l ⁻¹ .h ⁻¹		kinematic viscosity, at 100°F, cS	aromatics content, mmol/100 g	colour Saybolt	result "hot acid" test	result FDA test No. 121.1146
29	C	I	250	150	0.75	85	75	0.1	>+30	+	+
30	C	I	250	150	2.0	87	76	0.3	>+30	+	+
31	C	III	250	150	0.75	88	76	0.6	>+30	-	-
32	C	IV	250	150	0.75	83	68	1.0	>+30	-	-
33	C	V	250	150	0.75	89	77	0.8	>+30	-	+
34	C	VI	250	150	0.75	89	76	2.0	+27	-	-

WHAT WE CLAIM IS:—

1. A process for the preparation of medicinal oils, characterized in that a hydrocarbon mixture with an aromatics content of less than 10 %w is contacted at elevated temperature and pressure and in the presence of hydrogen with a catalyst containing one or more noble metals from Group VIII on a carrier, which carrier contains 13—15 %w of alumina, the remainder being silica.

2. A process according to claim 1, characterized in that the catalyst contains 0.05—5 %w of noble metal.

3. A process according to claim 2, characterized in that the catalyst contains 0.1—2 %w of noble metal.

4. A process according to any one of claims 1—3, characterized in that the catalyst contains platinum as noble metal.

5. A process according to any one of claims 1—4, characterized in that the catalyst has a surface area of 50—500 m²/g and a pore volume of 0.2—1.2 ml/g.

6. A process according to any one of claims 1—5, characterized in that the catalyst is prepared by impregnating a silica-alumina carrier with an aqueous solution containing



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one or more noble metals and drying and calcining the composition thus obtained.

7. A process according to any one of claims 1—6, characterized in that the catalyst is based on a silica-alumina prepared by precipitating alumina on a silica hydrogel and subsequently drying and calcining the material.

8. A process according to claim 7, characterized in that the catalyst is based on a silica-alumina prepared by starting from an aqueous silicate solution whose pH is reduced, as a result of which a silica hydrogel is precipitated, allowing the silica hydrogel to age, adding an aqueous solution of an aluminum compound, increasing the pH as a result of which alumina precipitates on the silica hydrogel, drying and calcining.

9. A process according to any one of claims 1—8, characterized in that the hydrocarbon mixture used as starting material for the process contains less than 25 wppm of sulphur.

10. A process according to any one of claims 1—9, characterized in that the catalytic hydrogen treatment is carried out at a temperature of 200—300° C., and a hydrogen partial pressure of 25—200 bar, a space velocity of 0.1—5 and preferably of 0.5—2 kg.l⁻¹.h⁻¹ and a hydrogen/feed ratio of 50—5000 Ni H₂/kg feed.

11. A process according to any one of claims 1—10, characterized in that the hydrocarbon mixture used as starting material for the process has a kinematic viscosity at 100° F. of at most 25 cS and that the catalytic hydrogen treatment is carried out at a temperature of 200—260° C. and a hydrogen partial pressure of 25—150 bar.

12. A process according to any one of claims 1—10, characterized in that the hydrocarbon mixture used as starting material for the process has a kinematic viscosity at 100° F. of more than 25 cS and that the catalytic hydrogen treatment is carried out at a temperature of 240—300° C. and a hydrogen partial pressure of 100—200 bar.

13. A process according to any one of claims 1—12, characterized in that the hydrocarbon mixture used as starting material for the process is a mineral oil distillate obtained in the distillation of a crude mineral oil at atmospheric or reduced pressure or a raffinate obtained in treating a mineral oil distillate with a selective solvent for aromatic hydrocarbons.

14. A process according to any one of claims 1—13, characterized in that the hydrocarbon mixture used as starting material for the process has first been subjected to a catalytic pretreatment with hydrogen using a sulphidic catalyst containing nickel and/or cobalt and in addition molybdenum and/or tungsten on a carrier.

15. A process according to claim 14, char-

acterized in that the catalyst applied in said pretreatment 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.

16. A process according to claim 14 or 15, characterized in that in the said pretreatment a catalyst is applied whose ratio by weight between nickel and/or cobalt on the one hand and molybdenum and/or tungsten on the other is between 1:1 and 1:10.

17. A process according to any one of claims 14—16, characterized in that in said pretreatment a catalyst is applied containing alumina as carrier.

18. A process according to any one of claims 14—17, characterized in that in said pretreatment a catalyst is applied which has been prepared by impregnation of 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.

19. A process according to any one of claims 14—17, characterized in that in said pretreatment a catalyst is applied which has been prepared by incorporating one or more nickel and/or cobalt compounds and one or more molybdenum and/or tungsten compounds in an alumina hydrogel, in a concentration sufficient to impart to the ready catalyst a metal content, expressed as metal oxides, of 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 after drying and calcination yields a xerogel with a bulk density of 0.75 to 1.6 ml/g and a pore volume of 0.15 to 0.5 ml/g.

20. A process according to any one of claims 14—17, characterized in that in said pretreatment a catalyst is applied which has been prepared by 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 hydrogen-sulphide-containing gas at a temperature below 150° C. and subsequently heating the material in a hydrogen-containing gas to a final temperature of above 200° C., the quantity of water present in the composition treated with the hydrogen-sulphide-containing gas corresponding to the quantity of water present in the composition after drying in a dry gas at 110° C., increased by 20—120% of the quantity of water which the dried composition can take up in the pores of the carrier at 20° C.

21. A process according to any one of claims 14—20, characterized in that the catalyst applied in said pretreatment contains fluorine.



22. A process according to claim 21, characterized in that the catalyst applied in said pretreatment contains 0.5—25 parts by weight and preferably 1—10 parts by weight of fluorine per 100 parts by weight of carrier.

23. A process according to claim 21 or 22, characterized in that more than 50% of the fluorine and preferably virtually all the fluorine present in the catalyst is incorporated therein by fluorination in situ.

24. A process according to any one of claims 14—23, characterized in that the hydrocarbon mixture used as starting material for the process, before said pretreatment has an aromatics content of less than 40 %w and an initial boiling point of above 200° C.

25. A process according to any one of claims 14—24, characterized in that said pretreatment is carried out at a temperature of 275—375° C., 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—5000 NI H₂/kg feed.

26. A process according to any one of claims 14—25, characterized in that the hydrocarbon mixture used as starting material for the process, before said pretreatment has a kinematic viscosity at 100° F. of at most 25 cS and that said pretreatment is carried out at a temperature of 275—350° C. and a hydrogen partial pressure of 25—125 bar.

27. A process according to any one of

claims 14—25, characterized in that the hydrocarbon mixture used as starting material for the process, before said pretreatment has a kinematic viscosity at 100° F. of more than 25 cS and that said pretreatment is carried out at a temperature of 325—375° C. and a hydrogen partial pressure of 75—200 bar.

28. A process according to any one of claims 14—27, characterized in that said pretreatment is carried out in such a manner that a liquid product containing less than 30 %w of components with a boiling point below the initial boiling point of the feed is formed.

29. A process according to any one of claims 1—28, characterized in that a medicinal oil is prepared meeting the UV absorption requirements of the British and/or German Pharmacopoeias.

30. A process for the preparation of medicinal oils, substantially as hereinbefore described with reference to any one of the foregoing Experiments Nos. 1—6, 15—20, 29 and 30.

31. A medicinal oil prepared by the process according to any one of claims 1—30.

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