PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the isomerisation of paraffin wax

We, NAAMLOOZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, 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:—

In Patent Specification No. 713,910 a process is claimed whereby paraffin wax is isomerised quite selectively and at a fast rate with the production of good yields of excellent lubricating oil and isoparaffin wax, which process comprises vaporising a paraffin wax and contacting the vapours, mixed with at least one mole of hydrogen per mole of said wax and in the absence of any liquid phase, with a supported platinum catalyst at a temperature between 300° and 550°C.

This process may be used for the isomerisation of any normally solid paraffin wax. The wax may be derived from mineral sources such as petroleum, oil shale, oil from tar sands, "Gilsonite" (Registered Trade Mark) and ozokerite, or may be a synthetic wax produced by the Fischer-Tropsch process or a by-product of other processes. The process may also be used for the isomerisation of crude so-called slack wax, refined waxes of various melting points or so-called residue wax. While the various waxes differ somewhat in properties, e.g. melting point and hardness, they are all composed of hydrocarbons containing long paraffinic chains. In some paraffin waxes the chains may be slightly branched and in some the chains may be attached to naphthenic or aromatic groups. Olefinic groups are rarely present; when present they do not affect the operation of the process. In any case, the paraffin chain of the wax molecules can be isomerised to give a product having a more highly branched structure.

In the process of Specification 713,910, the platinum catalyst may be applied on any of a number of conventional carrier materials commonly employed as supports for platinum catalysts. Alumina is a preferred support material, so-called activated alumina (gamma alumina) and activated bauxite being quite suitable. The alumina should be substantially free of alkaline materials, such in particular as the alkali and alkaline earth metals, and in order to insure the absence of any appreciable amounts of such alkaline materials in the catalyst and to promote the catalyst, it may be desirable to treat the carrier material with a halogen compound, e.g. HC1 or HF, prior to incorporating the platinum. The amount of platinum in the catalyst may vary from a few hundredths of one per cent, e.g. 0.05%, to about 1%, the preferred concentration being between about 0.1% and about 0.6%.

The platinum may be applied to the support in any one of several known ways. One suitable method is to impregnate the support material with a solution of a platinum salt, followed by drying and reducing in the conventional manner. Thus, for example, pellets of activated alumina may be treated with HF and then soaked in a solution of chloroplatinic acid, dried, and reduced in hydrogen at 475°C.

An essential feature of the process of Specification 713,910 is that the isomerisation is carried out in the presence of a large amount of hydrogen. The mole ratio of hydrogen to hydrocarbon is at least 1 and preferably above 5 and may be much higher, ratios above 300 being sometimes required in practical operation.

In carrying out the said process the wax is vaporised in a suitable vaporiser, mixed with the hydrogen, and the mixture is passed into contact with the catalyst, which is effected most conveniently by passing the vapour mixture through a bed of the catalyst supported in a reaction tube. The vapours issuing from the reaction tube are cooled to condense the product and the gas is then separated from the condensate. This gas is recycled. During repeated

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recycling of the gas the hydrogen gradually becomes diluted with inert gases produced by the minor amount of side reactions in the process. This is not particularly harmful as long as the specified minimum amount of hydrogen is applied. In order to prevent the dilution from becoming excessive, a small amount of the gas may be continuously withdrawn and replaced with fresh hydrogen.

The temperature in the catalyst bed is preferably between about 375°C and about 490°C. The operation may be carried out under reduced pressure, at atmospheric pressure, or at elevated pressures. Pressures between about 3.5 and 210 atmospheres are suitable, pressures of the order of 21 to 70 atmospheres being generally preferred. Under the conditions of temperature and pressure employed and in the presence of the large amount of hydrogen, the paraffin wax is retained in the vapour phase.

A contact time of the vapour mixture with the catalyst (calculated by dividing the volume of catalyst used by the volume of the vapour mixture contacting the catalyst per second) of only a tenth of a second is sufficient in many cases to afford a practical conversion. Longer contact times may, however, be used, particularly when operating at the lower temperatures. However, the contact time should not be so long at any given temperature as to cause excessive cracking. The contact time may usually be adjusted to between 0.5 and 25 seconds to afford the desired conversion, while limiting the formation of cracked products to below 25% and preferably below about 20%.

In Specification 713,910, it is essential that the processing conditions are such as to insure that the isomerisation reaction is carried out with the paraffin wax completely in the vapour phase, it having been found that if the wax was not completely vaporised in the reaction zone the process was inoperative.

Whilst the process of Specification 713,910 may be used for the isomerisation of the wide range of waxes mentioned, the process is difficult to carry out when it is desired to isomerise residue waxes and other such waxes having molecular weights above about 500, since such paraffin waxes are almost impossible to vaporise without decomposition. Thus, for example, in the isomerisation of bright stock wax, a ratio of hydrogen to wax of over 300 was necessary to insure the absence of a liquid phase in the reaction zone. If complete vaporisation was not maintained the small amount of liquid mist constituting the least volatile part of the wax collected on the catalyst, soaked into the particles thereof and was shortly converted into tarry deposits which blocked the catalyst surface.

It has now been found according to the present invention that the various paraffin waxes can be effectively and advantageously isomerised in the liquid phase and that in order to operate successfully in the presence of a liquid phase, it is essential that the wax be retained substantially completely in a liquid phase, i.e. the vaporisation of the wax must be repressed by the application of lower temperatures and/or lesser amounts of hydrogen. When the wax is substantially completely in the liquid phase, the relatively large amount of liquid wax apparently exerts sufficient dissolving and washing action to prevent blocking of the catalyst surface with tars. Also it is found that the isomerisation takes place at a slower rate in the liquid phase and that it is, therefore, necessary to employ longer contact times, viz. such of at least 5 minutes. In other respects the process is similar to the vapour phase process.

The present invention, which is a modification of the process claimed in Specification 713,910, therefore provides a process for the isomerisation of paraffin wax which comprises contacting said wax in the liquid phase, in the presence of at least one mole of hydrogen per mole of wax, with a supported platinum catalyst at a temperature between 300°C and 550°C for a contact time of at least 5 minutes. This contact time is calculated by dividing the volume of catalyst used by the volume of liquid wax passed in contact with the catalyst per minute.

Because of the large difference between the volume of a given amount of paraffin wax in the liquid phase and in the vapour phase and because of the smaller amount of hydrogen required, a reaction vessel of given size is capable of greater production capacity when operating according to the present invention with the wax substantially completely in the liquid phase than in the vapour phase process described in the aforesaid co-pending application.

The liquid phase process of the present invention is vastly superior to the vapour phase process of Specification 713,910 for the isomerisation of the higher molecular weight waxes (e.g. those having molecular weights above 500) and especially for the isomerisation of residual waxes, such as bright stock wax.

In the liquid phase isomerisation process of the present invention, any of the paraffin waxes mentioned above in connection with Specification 713,910 may be isomerised and the same platinum-containing catalysts are employed as are employed in accordance with Specification 713,910. The contact time, which should be at least five minutes, is preferably insufficient to produce more than 25% conversion to cracked products of low molecular weight. In order to reduce the occurrence of cracking reactions which is favoured by the longer contact times used in the process of the invention, and also in order to repress vaporisation, it is desirable to maintain the reaction temperature somewhat lower than the optimum temperature for vapour phase operation, namely between about 300°C and about 500°C, the preferred temperature being below about 490°C. The operation is preferably carried out under superatmospheric pressure, which may range between 3.5 and 210 atmospheres and is, for example above 7 atmospheres.

In the liquid phase process of the present invention, the presence of hydrogen in the reaction zone is essential, but the presence of a large amount of hydrogen is neither essential nor desired. Thus, mole ratios of hydrogen to paraffin wax between about 1 and 10 may be used. Such low ratios can only be approached in the vapour phase process when treating low molecular weight waxes that are easily vaporised.

In the liquid phase process of the invention the catalyst in the form of a powder may be slurried in the molten paraffin wax and the slurry may then be passed through a suitable reaction vessel while hydrogen is bubbled up through it, the catalyst being retained in suspension either by mechanical agitation or by agitation caused by the introduction of the hydrogen. Alternatively, the catalyst may be in the form of a fixed bed of pieces through which the molten paraffin wax is gradually passed from the bottom to the top concurrently with recycled hydrogen, or the molten wax may be allowed to trickle down through a fixed bed of pieces of the catalyst while hydrogen is passed through the bed either concurrently or countercurrently.

The products of the process of the invention are normally liquid oil, unconverted and partially converted wax, and a small amount of cracked products which latter may be distilled from the oil and wax. Depending upon the starting material and the degree of conversion, the total or distilled (as above) product may vary in consistency from a slurry or mush to a grease-like or plastic material. In some cases the product may be used as it is without any further processing. In other cases, particularly where a crude wax feed is used, it may be desirable to refine the product, for example, by extraction, clay treating or chemical treatment.

It will generally be desirable to separate the product obtained into two or more fractions. Thus, by employing conventional dewaxing techniques, a very high quality lubricating oil fraction may be separated. The pour point of the oil will depend in part upon the dewaxing conditions used and in turn the yield will depend in part upon the pour point chosen. Excellent yields of very low pour point oil of adequate viscosity for commercial usage and having a high viscosity index have been obtained from the product of a single pass isomerisation treatment. In view of its very low pour point and very high viscosity index, the oil is particularly suited for many special purposes such, for example, as refrigerator lubricating oil and low temperature hydraulic fluids.

The wax remaining after separating the oil consists of unconverted and partially converted wax and the mixture has a lower melting point and softer consistency than the starting material. It may be used as such or retreated to produce additional amounts of oil.

While the wax may be used as such or recycled, it may also be separated by known techniques into a fraction of partially converted wax and a fraction of unconverted wax. Either of these fractions may be recycled. Isoparaffin wax produced by the partial conversion of a wax consisting essentially of normal paraffin partakes somewhat of the characteristics of microcrystalline wax and may be used in place of microcrystalline wax. The isoparaffin wax differs from ordinary paraffin wax in having a much less brittle and more rubbery or plastic consistency. It resembles carnauba wax in its ability to absorb considerable quantities of oil without becoming sticky or tacky.

The amounts of the above products depend somewhat upon the character of the wax feed and largely upon the severity of the treating conditions (degree of conversion). When treating waxes under relatively mild conditions, only a small amount of oil is formed, whilst under more severe conditions the amount of oil is greatly increased, usually with more cracking.

The liquid phase process according to the invention is particularly advantageous for the isomerisation of high molecular weight waxes that are difficult or impossible to vaporise, for example so-called residue wax or bright stock wax. This wax, which is most difficult to treat in the vapour phase, yields novel and highly desirable lubricating oil. Also, when treating this high molecular weight material, a small to appreciable conversion to lower molecular weight products by hydrocracking which may occur is not detrimental as the resulting products are largely in the lubricating oil range; in fact, a highly desirable and novel light lubricating oil is produced.

The lubricating oils produced by the process of the invention possess highly desirable properties. When starting with a paraffin wax obtained from a first dewaxing step and consisting almost completely of straight-chain paraffin hydrocarbons, the lubricating oils produced consist largely of isoparaffin hydrocarbons. While these isoparaffins have a branched structure, they do not have the complicated structure obtained by the polymerisation of olefins, e.g. isobutylene, and, consequently, they are more thermally stable. While these lubricating oils consist largely of isoparaffins they also contain appreciable amounts of aromatic constituents, especially when the oils are produced from residue waxes.

When starting with a residue wax, such as bright stock wax, the lubricating oils produced also differ from those produced by other methods and consist predominantly of hydrocarbons having a cyclo-paraffin nucleus with attached long isoparaffin side-chains and also contain appreciable amounts of hydrocarbons having an aromatic nucleus.

The invention is further illustrated by the following examples, in which the percentages are percentages by weight, the space velocity is the volume of wax processed per volume of catalyst per hour and the contact time is the reciprocal of the space velocity, given in minutes.

EXAMPLE I

A hard, white, heavy distillate paraffin wax having the following properties:

Melting Point	ca 70°C
Molecular Weight	ca 500
n-Paraffin content	ca 90%

was isomerised in the liquid phase, using a platinum-alumina catalyst containing 0.3% platinum. The operating conditions and results are shown in the following table:

Temperature, °C	400	450	475
Pressure, atm.	35	35	35
Space velocity	2.5	5.1	5.2
H_2/Feed, Mole Ratio	15	15	15
Contact Time (minutes)	24	11.8	11.5
Products			
Gas + Loss, %	4.0	5.0	7.0
Distilling below 300°C, %	4.2	10.8	23.1
Distilling above 300°C, %	91.8	84.2	69.9
Analysis of product distilling above 300°C			
Aromatics, %	6.4	12.5	19.7
Liquid Saturates, %	26.3	24.9	37.1
Wax, %	59.0	46.8	13.0
Aromatic content of Oil distilling above 300°C, %	19.5	33.4	34.8
Properties of Light Oil (distilling 300-400°C)			
Viscosity, 37.7°C, centistokes		4.61	4.05
Viscosity, 99°C, centistokes		1.61	1.46
Viscosity Index		112	106
Pour Point, °C		+4	−10
Properties of Heavy Lubricating Oil			
Viscosity, 37.7°C, centistokes	19.8	24.20	21.33
Viscosity, 99°C, centistokes	4.37	4.82	4.36
Viscosity Index	138	136	131
Pour Point, °C	−29.5	−37	−37

EXAMPLE II

Bright stock wax is the very high molecular weight wax obtained from the residue remaining after distilling off the distillable lubricating oil fractions from a lubricating oil petroleum stock. The non-distillable oil (bright stock) in this residue is particularly desired for certain purposes and is in demand. A bright stock wax having the following inspection data:

Density, g/ml. at 20°C	0.8899
Viscosity at 99°C (A.S.T.M. D-445)	20.50
Molecular Weight	717

was isomerised in the liquid phase.

The operating conditions and results are shown in the following table:

Temperature, °C, Max.	423	410	405	385
Pressure, atm.	35.3	35.3	35.1	35
H_2/Feed Mole Ratio	6.9	4.7	4.7	4.7
Space Velocity	1.6	2.3	2.3	2.3
Contact Time (minutes)	37.5	26	26	26
Light Lubricating Oil				
% of Charge	20.7	11.5	8.7	3.0
Viscosity, centistokes at 37.7°C	14	13	29	23
Viscosity Index	115	122	116	113
Pour Point, °C	−7	−7	−4	−7
Heavy Lubricating Oil				
% of Charge	20.3	20.6	20.6	21.3
Viscosity, centistokes at 37.7°C	244	338	366	404
Viscosity Index	102	93	93	90
Pour Point, °C	−10	−4	−5	−4

What we claim is:—

1. A process for the isomerisation of paraffin wax, which comprises contacting said wax in the liquid phase, in the presence of at least one mole of hydrogen per mole of wax, with a supported platinum catalyst at a temperature between 300°C and 550°C, for a contact time of at least 5 minutes.

2. A process as claimed in claim 1, wherein the temperature is between 300°C and 500°C.

3. A process as claimed in claim 1 or 2, wherein the contact time is insufficient to produce more than 25% conversion to cracked products of lower molecular weight.

4. A process as claimed in claim 1, 2 or 3, wherein the reaction is carried out under super-atmospheric pressure.

5. A process as claimed in claim 4, wherein the pressure is between 3.5 and 210 atmospheres.

6. A process as claimed in any one of the preceding claims, wherein about 1 to 10 moles of hydrogen per mole of paraffin wax are used.

7. A process as claimed in any one of the preceding claims wherein hydrogen-containing gas is separated from the reaction product and is recycled.

8. A process as claimed in any one of the preceding claims, wherein the reaction product is distilled to remove cracked products.

9. A process as claimed in claim 8, wherein the residue remaining after distilling off the cracked products is dewaxed to separate a lubricating oil of low pour point and high viscosity index.

10. A process as claimed in claim 9, wherein bright stock wax is converted to bright stock.

11. A process as claimed in any of the preceding claims applied to a wax having a molecular weight above 500.

12. A process for the isomerisation of paraffin wax and for the production of lubricating oil substantially as hereinbefore described with particular reference to the examples.

13. Lubricating oils having a low pour point and high viscosity index prepared by isomerising paraffin wax by the process claimed in any of the preceding claims.

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number of conventional carrier materials commonly employed as supports for platinum cata-

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ERRATUM

SPECIFICATION NO. 755,105

In the heading on page 1,

for "(Patent Addition to No. 71390 dated Aug. 12, 1952)"

read "(Patent of Addition to No. 713910 dated Aug. 12, 1952)"

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17th September, 1956

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wax may be derived from mineral sources such as petroleum, oil shale, oil from tar sands, "Gilsonite" (Registered Trade Mark) and ozokerite, or may be a synthetic wax produced by the Fischer-Tropsch process or a by-product of other processes. The process may also be used for the isomerisation of crude so-called slack wax, refined waxes of various melting points or so-called residue wax. While the various waxes differ somewhat in properties, e.g. melting point and hardness, they are all composed of hydrocarbons containing long paraffinic chains. In some paraffin waxes the chains may be slightly branched and in some the chains may be attached to naphthenic or aromatic groups. Olefinic groups are rarely present: when present they do not affect the operation of the process. In any case, the paraffin chain of the wax molecules can be isomerised to give a product having a more highly branched structure.

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