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ISOMERIZATION OF PARAFFIN WAX

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This invention relates to a new and useful process for the isomerization of paraffin wax. The invention also relates to a process for the production of lubricating oil and isoparaffin wax from paraffin wax.

Paraffin wax is a normally solid wax-like substance composed of high molecular weight hydrocarbons. It is usually obtained from the heavier fractions of petroleum such as are used for the production of lubricating oils as well as certain burning oils. In nearly every case, it is an undesired constituent in such oils and is removed by known so-called dewaxing methods during refining. While paraffin wax is useful for many purposes such as sealing containers, production of waxed paper, production of water-proofed cartons and the like, and finds a large and wide use, there is still a considerable amount of paraffin wax for which there is no ready market.

Various processes have been proposed for the treatment or conversion of paraffin wax. Those processes resulting in a hydrocarbon product generally involve a refining operation which produces a normally solid wax of improved characteristics, or a more drastic conversion treatment which results in the production of a liquid product. The former usually comprises such steps as solvent extraction, fractional crystallization, clay treatment and the like, in which the structure of the hydrocarbons is unaltered. The latter involves a step in which the hydrocarbons are decomposed or split to give a wide range of products comprising normally gaseous and normally liquid products, most of which are of relatively low value. It would be most advantageous to have a practical process whereby paraffin wax could be converted into more valuable hydrocarbon products. One possibility lies in isomerization.

By isomerization of paraffin wax is meant the treatment of the wax under conditions to isomerize the hydrocarbon constituents into isomers having the same molecular weight but a more branched structure. Some isomerization may take place in other drastic conversions of the wax but the term "isomerization process" is considered to designate only a process in which such isomerization to a more branched structure takes place to a substantial extent without more than a minor occurrence of other reactions. In the isomerization process, therefore, no appreciable amount of hydrogen is removed from the wax and the molecular weight of the product is substantially the same as that of the starting material.

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It is known that the melting points of the wax hydrocarbons are lowered upon isomerization to isomers having a more branched structure. Merely by way of example, normal hexacosane, a typical wax constituent, is a waxy solid having a melting point of 56° C. whereas, its isomer 6,6 dipentyl hexadecane is a normally liquid compound having a melting point of -40° C. Thus, by suitable isomerization a substantial conversion of even high molecular weight paraffin wax to a normally liquid product may be obtained. This liquid product is an oil having particularly desirable properties. The isomerization can be accomplished and has been accomplished as described in U. S. Patent No. 2,475,358.

The main difficulty encountered in attempts to isomerize paraffin wax is in preventing excessive degradation (cracking) to lower molecular weight products of little value. It is well known and generally recognized that the tendency for hydrocarbons to crack increases rapidly with increasing molecular weight. This holds both for thermal cracking as well as cracking induced by a cracking catalyst. Thus, whereas normal butane may be converted to isobutane quite selectively, the selective isomerization of paraffins of higher molecular weight becomes increasingly difficult as the molecular weight is increased. In the method described in U. S. Patent No. 2,475,358, a fairly selective isomerization of paraffin wax is obtained by the use of Friedel-Crafts-type catalyst which has been modified to decrease its cracking tendency and by simultaneous use of a large amount of a cracking-suppressor (decahydronaphthalene). While this method affords a moderate yield of lubricating oil of high viscosity index, and also diesel fuel of good cetane number, the recovery of the product requires special steps, and some catalyst is lost in each cycle. The process also involves the handling of corrosive liquids, and the isomerization reaction is intrinsically slow so that large reactors are required.

It has now been found that paraffin wax may be isomerized quite selectively and at a much faster rate with the production of good yields of excellent oil and isoparaffin wax by a new process which is quite simple and in which no corrosive reagents are involved. In this process the paraffin wax is isomerized by treatment in the vapor phase with a platinum-containing catalyst. The various details of the process are described in the following:

The process of the invention is applicable for the isomerization, as defined above, of any normally solid paraffin wax. The wax will usually

be derived from mineral sources such as petroleum oil shale, oil from tar sands, gilsonite, ozokerite, or the like, as well as from coal via extraction and/or hydrogenation processes, but paraffin wax produced by the Fischer-Tropsch synthesis or as a by-product of other processes may also be isomerized. The process may be applied for the isomerization of crude so-called slack wax or to refined waxes of various melting points. While the various crude waxes and refined 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 may have naphthenic or aromatic groups attached. Olefinic groups are rarely present. When present they will not affect the operation of the process. In any case, the paraffin chain of the wax molecules can be isomerized to give a product having a more highly branched structure.

In the process of the invention, the paraffin wax is isomerized through the aid of a supported platinum catalyst. Palladium or nickel may be substituted for platinum if desired. The platinum may be applied on a number of conventional carrier materials hitherto employed as a support for platinum catalyst. Suitable supports are described in U. S. Patents Numbers 2,478,916 and 2,550,531. Alumina is a preferred support material. So-called activated alumina (gamma alumina) and activated bauxite are quite suitable. The alumina should be substantially free of alkaline materials such in particular as the alkali and alkaline earth metals. In order to insure the absence of any appreciable amounts of such materials in the catalyst, it may be desired to treat the carrier material with acid, e. g., HCl or HF, prior to incorporating the platinum. The amount of platinum in the catalyst may vary from a few hundredths of a per cent, e. g., 0.05% to about 1%. The preferred concentration of platinum is 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 soaked in a solution of chloroplatinic acid, dried, and reduced in hydrogen at 475° C. Commercial "0.5% platinum on alumina pellets" made by Baker and Company, Inc., Newark, New Jersey, can be used.

An essential feature of the method of the invention is that the isomerization is carried out in the presence of a large amount of hydrogen. The mole ratio of hydrogen to hydrocarbon should be at least 1 and preferably above 5 and may be much higher. However, in practical operation, the ratio will rarely exceed about 300.

In carrying out the process, the wax is vaporized in a suitable vaporizer, mixed with the hydrogen, and the mixture is passed into contact with the catalyst. The hydrogen may advantageously be passed through the vaporizer to aid in the vaporization. The contact is most conveniently effected by supporting a bed of the catalyst in a reaction tube and passing the vapor mixture through the bed. Other methods of contact may, however, be applied if desired. The vapors 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 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 bed is between 300° C. and 550° C. and is preferably between about 375° C. and about 490° C. The operation may be carried out under reduced pressure, at atmospheric pressure, or at considerably elevated pressures. Pressures between about 50 and 3000 p. s. i. g. are suitable, pressures of the order of 300-1000 p. s. i. g. being generally preferred.

Under the conditions of temperature and pressure employed and in the presence of the large amount of gas the wax is retained in the vapor phase. It is essential that no condensation to a liquid take place in the reaction zone.

Under the described conditions, the isomerization takes place at a very rapid rate. Thus a contact time of the vapor mixture with the catalyst of only a tenth of a second is sufficient in many cases to afford a practical conversion. It is evident that with such rates a small reactor is capable of handling a large throughput. 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 to cause excessive cracking. The contact time may usually be adjusted between 0.5 and 25 seconds in any case to afford the desired conversion while limiting the formation of cracked products to below 25% and preferably below about 20%.

When treating a paraffin wax under the conditions above described, the product consists of normally liquid oil, unconverted wax, partially converted wax, and a small amount of cracked products. The small amount of cracked material 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 is without any further processing. In other cases, particularly where a crude wax feed was used, it may be desirable to refine the product by extraction, clay treating, chemical treatment or the like.

While the product may find application without further refinement, it will generally be desirable to separate it 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 isomerization 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, low temperature hydraulic fluid, and in the production of low temperature greases.

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 paraffins 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; when treating under more severe conditions the amount of oil is greatly increased, usually with more cracking.

The following examples are illustrative of the invention and the effect of the severity of the processing conditions.

Example I.—A paraffin wax having the following properties was isomerized:

Melting point, AMP	° F	138-140
Average molecular weight	ca.	385
$d_{60/4}^{\circ} C$		0.7786
$n_{60}^{\circ} C/D$		1.4356
$n_{70}^{\circ} C/D$		1.4325
$n_{80}^{\circ} C/D$		1.4293

The isomerization was effected by vaporizing the wax with from 52 to 63 moles of hydrogen per mole of wax and passing the vapor mixture through a bed of platinum-alumina catalyst containing about 0.3% platinum under the following reaction conditions:

Temperature	° C	430
Pressure	p. s. i. g.	500
Space velocity ¹		25.4

¹ Space velocity is defined as the volumes of wax processed per volume of catalyst per hour.

The losses, including the small amount of cracked products, amounted to about 2.4% of the wax feed. The product was refined by a series of dewaxing steps to separate narrow fractions of the oil produced. The amounts and properties of the oil fractions are shown in the following table:

Fraction	Yield Percent/ Wt. of Feedstock	Viscosity, cs.		Vis- cosity Index	Pour Point, ° F. (ASTM)	η_{sp} at 70° C.
		100° F.	210° F.			
A	5.6	12.02	3.16	144	-15	1.4332
B	1.6	12.50	3.00	105	+5	1.4474
C	2.2	11.34	3.15	160	+25	1.4325
D	5.6	11.79	3.29	169	+60	1.4322

Since the conditions were in this case very mild due to the very high space velocity (calculated contact time, 0.77 second) the conversion was quite limited. It will be noted, however, that 15% by weight of the wax was converted to oil of which about 37% was an oil of viscosity suitable for low temperature applications, very high viscosity index, and below zero Fahrenheit pour point. This desirable oil could be separated and the remaining oil recycled with or without the

unconverted and partially converted wax. This operation is attractive because the throughput is very high and the losses to cracking are very low.

Example II.—A wax having the properties shown above was isomerized under the same conditions, except that the space velocity was 6.8. The losses, including losses to cracked products, amounted to about 5.6% by weight. The product was refined as before to give the following yields of oil fractions:

Fraction	Yield Percent/ Wt. of Feedstock	Viscosity, cs.		Vis- cosity Index	Pour Point, ° F. (ASTM)	η_{sp} at 70° C.
		100° F.	210° F.			
A	25.4	11.62	3.03	134	-55	1.4330
B	5.3	8.03	2.28	105	-20	1.4460
C	10.7	11.30	3.12	154	+5	1.4317
D	13.7	11.75	3.27	163	+65	1.4315

It will be seen that at the somewhat more severe conditions the yield of oil was increased to 55% by weight and that more than half of the oil was lubricating oil of especially desirable properties. The unconverted and partially converted wax, amounting to 39% of the feed, could be recycled.

Example III.—The same wax was isomerized under the same conditions at a space velocity of 2.3. Under these more severe conditions the losses, including the loss through cracked products, amounted to about 18% by weight. The product was refined as before to give the following yields of oil:

Fraction	Yield Percent/ Wt. of Feedstock	Viscosity, cs.		Vis- cosity Index	Pour Point, ° F. (ASTM)	η_{sp} at 70° C.
		100° F.	210° F.			
A	6.6	6.55	1.95	89	-70	1.4551
B	37.8	11.01	2.89	127	-60	1.4326
C	10.7	11.01	3.04	152	-10	1.4512
D	9.8	11.10	3.14	164	+45	1.4310

It will be seen that in this case the yield of valuable lubricating oil was again greatly increased with a relatively small increase in cracked products.

The above examples illustrate on a readily comparable basis the effect of the severity of the conditions upon the yields obtained. It is to be understood that the severity of the conditions may also be altered by changing other factors than the space velocity, e. g., the temperature and/or pressure.

Example IV.—A white, hard, heavy distillate wax having the following inspection data was isomerized:

Melting point, ° F., A. S. T. M.	161
Gravity A. P. I., 210° F.	51.8
Refraction index, 80° C/D	1.4376
Oil content, A. S. T. M. D-721, percent	0.87
Molecular weight	522
Viscosity, SSU at 210° F.	50.6

The wax was vaporized and isomerized under the following conditions:

Temperature	° C	404-440
Pressure	p. s. i. g.	250
Space velocity		5.12
Hydrogen/feed mole ratio		33

There were obtained 74.5% of a wax of soft consistency containing lubricating oil, the amount of which is to be determined; 33.4% of a distillate fraction boiling up to 150° C. at 5 mm. pressure and containing light lubricating oil; 2.7% of light

ends due to cracking; and 3.7% of gas plus experimental loss.

Example V.—Bright stock wax is the very high molecular weight wax obtained from bright stock, which is the residue remaining after distilling off the lubricating oil fractions from a lubricating oil petroleum stock. The oil portion of bright stock is particularly desired for certain purposes and is in demand. A bright stock wax having the following inspection data was isomerized.

Density, g./ml. at 20° C. 0.8899
 Viscosity at 210° F., A. S. T. M. D-445 20.50
 Molecular weight 717

The wax was vaporized with hydrogen and isomerized under the following conditions:

Temperature ° C. 418-421
 Pressure p. s. i. g. 300
 Space velocity 1.66
 Hydrogen/feed, mole ratio 336

There were obtained 71.9% of a very soft wax containing bright stock, the amount of which is to be determined; 20.8% of a distillate fraction boiling up to 238° C. at 3 mm. pressure, and containing lubricating oil; and 7.3% of gas plus experimental loss. The soft wax was found to give a lower coefficient of friction than the starting wax and in view of its softer consistency is better suited as a rolling lubricant.

We claim as our invention:

1. The process for the isomerization of paraffin wax which comprises vaporizing a normally solid paraffin wax and contacting the wax completely in the vapor phase with at least one mole of hydrogen per mole of said wax with a supported platinum catalyst at a temperature between about 300° C. and about 550° C.

2. A process according to claim 1 in which the platinum is supported on an alkali-free alumina.

3. A process according to claim 1 in which the said vapors are contacted with the said catalyst under a pressure between about 50 and 3000 pounds per square inch in the presence of sufficient recycle gas that condensation to the liquid phase is avoided.

4. A process for the production of a lubricating oil having low pour point and high viscosity index from paraffin wax which comprises vaporizing a normally solid paraffin wax with recycle gas containing at least one mole of hydrogen per mole of said wax, contacting the mixture completely in the vapor phase with a supported platinum catalyst at a temperature between about 375° C. and about 490° C. and under a pressure between about 50 and 3000 p. s. i. for a time between 0.5 second and 25 seconds insufficient to produce more than 25% conversion to cracked products of lower molecular weight, cooling the gaseous product, separating and recycling the hydrogen-containing gas, distilling from the product the small amount of normally liquid cracked products, and subjecting the remainder to a dewaxing treatment to separate the normally liquid oil having the designated properties.

5. A lubricating oil prepared by the process of claim 4.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,475,358	Moore et al.	July 5, 1949