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(12) **Patent:**

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(54) ISOMERIZATION OF PARAFFIN WAXES

(54) ISOMERISATION DE CIRES DE PARAFFINE

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ABSTRACT:

CLAIMS: [Show all claims](#)

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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This invention relates to the isomerization of paraffin waxes by treatment at elevated temperatures with solid catalysts in the presence of hydrogen. More particularly the invention relates to an improvement in the isomerization of such paraffin waxes in the liquid phase.

Paraffin wax is a normally solid wax-like substance composed of high molecular weight hydrocarbons. It is called paraffin wax to distinguish it from the vegetable and animal waxes which are composed largely of oxygenated compounds. Paraffin wax 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.

It has been recently discovered that paraffin waxes may be converted to valuable oils by catalytically treating them at suitable high temperature conditions in the presence of hydrogen. Thus, the treatment of paraffin waxes in the vapor phase with a platinum, nickel, or palladium catalyst in the presence of hydrogen is disclosed in U.S. Patent 2,668,866. Along with the isomerization of the wax to oil, appreciable amounts of light oil of the nature of diesel fuel are usually produced. Also a disadvantage of the process is that it is very difficult to maintain the usual paraffin waxes completely in the vapor phase. In U.S. Patent 2,668,790, it is shown that the paraffin waxes may be isomerized in the liquid phase under hydrogen pressure. This overcomes the problem involved in maintaining the wax in the vapor state but has the disadvantage that the reaction time must be considerably increased. Thus, contact times of at least five minutes are required. These longer contact times tend in general to favor undesired cracking reactions. In general, the liquid phase operation is carried out by passing the liquid wax and hydrogen up through a fixed bed of the catalyst. In this way the longest contact time is

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obtained with a given volume of catalyst. However, it is also possible to allow the molten wax to trickle down through a fixed bed of pieces of the catalyst while the hydrogen is passed through the bed either concurrently or countercurrently.

When operating in this latter manner the rate of flow of the molten wax through the catalyst bed is a function of the wax input rate expressed in terms of volumes of liquid wax per unit of area of horizontal cross-section of the catalyst bed per unit of time. As the input rate is decreased the film of molten wax decreases in thickness and flows at a decreased linear velocity. With catalyst particles of the usual size range, e.g., 2 - 8 mm average diameter and an input rate of 1 cc per second per square inch, the linear flow velocity is about 4 cm per second. On the other hand, if the film thickness is increased by the application of such liquid loadings the rate of reaction drops off markedly and the life of the catalyst is shortened. This is due to the lesser accessibility of the protective hydrogen to the catalyst surface which is covered with the molten wax. For this reason it has been the practice to use relatively shallow beds of catalyst with low liquid loadings of the order of 0.13 to 0.33 cc of molten wax per second per square inch. Such low liquid loading gives a thin slowly moving film of the molten wax through which sufficient hydrogen can penetrate to the catalyst surface.

It is now found that high conversions of paraffin wax may be obtained at much higher liquid loadings while at the same time also retaining the activity of the catalyst. This is accomplished by passing hydrogen-containing gas concurrently downward through the catalyst bed at a relatively high rate compared to the normal trickle rate of the liquid wax under equivalent loading. It is found that when the linear flow of the gas is about twice or more the normal trickle rate, the film of liquid wax does not obtain such thickness that conversion and catalyst

life are adversely affected. Thus, it is possible to apply much higher liquid loadings.

The liquid loading, although high, must be maintained below the point of flooding. With catalyst of the usual particle size range, flooding occurs at a liquid loading of about 10 cc per second per square inch. The liquid loadings when operating according to the present method may range from about 1.5 cc per second per square inch up to the flooding point or about 10 cc per second per square inch. In these cases the normal trickle rate of the liquid oil is from about 5 to about 9 cm per
10 second. The gas rate is therefore adjusted such that the linear velocity is at least 10 cm per second in the first instance and at least 18 cm per second in the second instance. These are however the lower limits, and higher velocities may be and generally are applied. Thus, gas flow rates at least three times the normal trickle velocity are to be recommended. For instance, in a typical case a gas rate of 16 cm per second is employed with a liquid loading of 1.64 cc per second per square inch.

The gas flow rate is calculated using as the traversed volume the free volume (interparticle space) of the catalyst bed (which is substantially independent of the size of the catalyst particles so long as
20 they are uniform and is generally about 45% of the volume of the catalyst bed), as the traversed distance the vertical height of the catalyst bed, and as the volume of gas the actual volume of gas withdrawn from the reactor corrected for the reaction temperature and pressure according to the ideal gas laws. It will be apparent that the actual gas velocities are considerably greater than those calculated due to the tortuous path that the gas traverses. It is necessary however to rely upon the calculated value since the actual velocity varies from point to point depending upon the packing and is not believed capable of direct determination or reliable calculation.

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The importance of maintaining a very thin film of the liquid wax when employing high liquid loadings is illustrated by the following comparative tests.

At the same throughput rate expressed in terms of liters of molten wax per liter of catalyst per hour, and under the same conditions of temperature and pressure, a molten paraffin wax was isomerized to lubricating oil by passing it with gas consisting mainly of hydrogen through a bed of pelleted hydroisomerization catalyst. In the first case where the film was thick, over 10% by weight of the wax was cracked to lower boiling products (boiling below 300°C) while the yield of oil after dewaxing the product was 30.5% by weight based on the wax feed. After an operating period of 132 hours the activity of the catalyst had dropped so that the oil yield had fallen to 25.9% by weight. In the second case where the film of oil was maintained thin, the amount of wax cracked to lower boiling products (boiling below 300°C) was 6% by weight while the yield of oil was 50.5% by weight. The conversion efficiency was 88.4%. After 135 hours of continuous operation the catalyst had not been impaired at all.

The wax used in the above examples had a melting point of 54.3°C, an average carbon number of 27, boiled above 300°C, and contained 4.7% oil as determined according to ASTM Method D721-51T. The operation was carried out at 420°C and 35 atmospheres pressure. The oil products were obtained by dewaxing at -5°C in a liquid medium consisting of 5 parts by weight of methyl ethyl ketone to 1 part by weight of the product. The oil obtained in the latter operation had a pour point of 8°C, a viscosity index of 155, a viscosity at 100°F of 11.7 cs, and at 210°F of 3.2 cs.

Paraffin waxes may be isomerized according to the present process at temperatures between about 350°C and about 440°C and preferably between 400°C and 440°C. The pressure may vary from about 25 atmospheres to about 200 atmospheres, although pressures between 25 atmospheres

and about 40 or 50 atmospheres are most suited and generally employed. The mole ratio of hydrogen to hydrocarbon is sufficient to afford the specified velocities and is in any case at least 10.

The process is applicable with any of the solid catalysts which have hydrogenation-dehydrogenation properties in conjunction with isomerization activity. In addition to platinum or nickel on a carrier of acid nature, such as alumina promoted with fluorine, various other catalysts may be employed. In place of platinum, the metals of the left hand column of the Sixth Group of the Periodic System and those of the Eighth Group of the Periodic System and their various hydrogenating-dehydrogenating compounds such as the oxides, sulfides, etc., may be employed. The acid carrier for these various hydrogenation-dehydrogenation promoters may be natural or artificial alumina promoted with minor amounts of halogen, preferably fluorine, or such acid materials as the various clay-type cracking catalysts, including the so-called natural catalysts (acid treated clays), as well as various synthetic composites such as silica-alumina, silica-magnesia, silica-alumina-zirconia, alumina-boric oxide, and silica-aluminum phosphate. In addition to the above-mentioned platinum and nickel catalyst supported on halogen promoted alumina, the following catalysts are especially suited: platinum-molybdenum oxide on alumina promoted with fluorine, nickel sulfide-tungsten sulfide on alumina promoted with fluorine, molybdenum oxide on alumina promoted with fluorine, and molybdenum oxide supported on alumina-boric oxide.

As compared with the liquid phase treatment carried out in the conventional way, considerably higher yields of isomerized product are obtained by means of the process according to the invention, while cracking reactions leading to the formation of the products of lower molecular weight only occur to a slight extent. The conversion efficiency, that is the percentage by weight of isomerized product with respect to the total quantity of the feed material converted, is therefore also considerably

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higher. Thus, when isomerizing paraffin waxes of high molecular weight (average molecular weight of more than 350 and boiling above 300°C) and applying optimum conditions indicated above, yields of more than 40% by weight, calculated on the feed material, of oil product boiling above 300°C can be obtained per passage over the catalyst while the quantity of cracked products boiling below 300°C is only slight, e.g., below 10% by weight. Thus, the conversion efficiency is generally of the order of 85 to 90%.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In the isomerization of a paraffin wax by contacting the same in the presence of added hydrogen with a solid isomerization catalyst containing a hydrogenation promoter at a temperature between about 350°C and about 440°C and a pressure between about 25 atmospheres and about 200 atmospheres, the improvement which comprises passing the wax in the liquid state downward through a foraminous bed of the catalyst at a rate between 1 and 10 cc per second per square inch of cross-section of the catalyst bed while passing hydrogen-containing gas downward through said bed concurrently at such a rate that the linear velocity of flow of the gas under the processing conditions is at least twice the normal linear flow rate of the liquid wax at the same liquid loading whereby the thickness of the film of wax on the catalyst is reduced sufficiently that substantial conversion of the wax without impairment of the catalyst activity is obtained at said high liquid loadings.

2. The process according to claim 1 further characterized in that the said linear velocity of flow of the gas under processing conditions is at least 3 times the normal rate of flow of the liquid wax at the same liquid loading.