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(12) **Patent:**

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(54) PROCESS FOR ISOMERIZING WAXY HYDROCARBONS

(54) PROCÉDE POUR L'ISOMÉRISEMENT D'HYDROCARBURES CIREUX

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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 waxy hydrocarbons, particularly to the application of special catalysts and special reaction conditions which ensure an improved method of carrying out the isomerization. The invention more particularly relates to the production of especially high grade lubricating oils from paraffin waxes by catalytic isomerization with a minimum of cracking and in a more practical and economical manner.

Paraffin wax is the wax 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 all cases, it is an undesired constituent of such oils and is removed by known so-called dewaxing methods during refining. It is a normally solid wax-like substance composed of high molecular weight hydrocarbons and is called paraffin wax to distinguish it from the vegetable and animal waxes which are composed largely of oxygenated compounds.

Various processes have been proposed for the treatment or conversion of paraffin wax. The processes resulting in a hydrocarbon product generally involve a refining operation which produces a normally solid wax of improved characteristics, or involve a more drastic conversion treatment which results in the production of a liquid product. The former usually comprises such steps as hydrogenation, solvent extraction, clay treatment, and the like, in which the structure of the hydrocarbons and the melting point of the wax are substantially unaltered. The latter processes involve a step in which the hydrocarbons are decomposed or split to give a range of products comprising normally gaseous and normally liquid products, most of which are of relatively low value.

It is already known to subject paraffin wax to an isomerizing treatment in order to convert the normal or branched alkane groups

present therein into branched or more highly branched structures. Also, it is known that by effecting such isomerization in a selective manner, i.e., with little or no cracking, the isomerized product is a lubricating oil of unique and exceptionally desirable properties.

According to U.S. Patent specification 2,475,358, isomerization is carried out by treating the starting material in the liquid phase, for example, at a temperature from 80°C to 110°C, in the presence of a hydrocarbon-aluminum halide-complex, e.g., a toluene-aluminum chloride complex; in this case, isomerization only takes place slowly while, in order to inhibit pronounced decomposition of the starting material, the process must also be carried out in the presence of certain substances which act as cracking inhibitors.

More recently, it was found that a superior oil may be produced from normally solid paraffin waxes by passing the latter in the vapor or liquid form together with at least one mole of hydrogen per mole of paraffin wax into contact with a catalyst applied to a carrier and which contains not more than 1% by weight of platinum at a temperature between 300°C and 550°C and under reduced, atmospheric, or increased pressure. This is described and claimed in U.S. patents 2,668,790 and 2,668,866, both issued February 9, 1954.

Although good results may be obtained by platinum-containing catalysts, the disadvantage is that platinum is very sensitive to poisoning, is of comparatively rare occurrence, and is very costly.

Attempts have been made to find a cheaper catalyst which is easier to handle and which meets the requirement of a highly selective isomerizing effect, thereby ensuring good isomerization

without pronounced decomposition of the hydrocarbons accompanied by the formation of products with a lower molecular weight simultaneously taking place. It is known (e.g., U.S. Patent specification 2,063,625) that lubricating oils of fair viscosity index can be produced from normally solid paraffin wax by treating the wax at a temperature between 200° and 450°C in an atmosphere of nitrogen or cracked gases containing olefins and hydrogen under pressure with catalyst comprising various elements of the 5th to the 8th group of the Periodic System such as molybdenum, tungsten, chromium, 10 sulfur, vanadium, manganese, nickel, cobalt, iron, mixtures of these or their compounds as, for example, oxides or sulfides, e.g., molybdena deposited upon activated carbon. The presence of a catalyst having a strong condensing action such as aluminum chloride, zinc chloride, or the like, is also recommended. In the absence of the condensing catalyst a light oil of the nature of spindle oil is produced along with copious quantities of cracked gases. When the strong condensing catalyst is also present a more viscous liquid is produced, presumably by the condensation and polymerization of olefins and other products of the cracking. The oil produced by 20 this process is not the desired super oil but an aromatic oil having a high density and lower molecular weight than the paraffin wax from which it is produced. Also, the process has the severe disadvantage from the practical standpoint of being inordinately slow. Thus, reaction times from 1/2 to 6 hours, and generally of the order of 2 hours are required. This, coupled with the considerable loss of product into gas and other cracked products, allows only a small production capacity.

We have now found that normally solid paraffin waxes may be isomerized to lubricating oils in a much faster and more economical

rate corresponding to reaction times of 0.5 to 6 minutes, provided that a special catalyst is used. However, in order to avoid cracking and thereby produce the desired oil of high quality with this catalyst, it is essential that the processing condition be carefully chosen.

The catalyst used in the process of our invention comprises molybdenum, aluminum, and combined fluorine. It is found that these ingredients are essential to the proper functioning of the catalyst and that in addition, the ingredients should be properly combined in
10 suitable balance. The molybdenum, calculated as MoO_3 , should constitute at least 7 parts by weight in the form of the oxide or sulfide per 100 parts by weight of the alumina, and preferably about 11 parts. The fluorine should constitute less than 5% by weight and preferably less than 1% by weight, e.g., about 0.5% by weight. The fluorine is combined in the catalyst and is tenaciously held therein. However, the exact nature of its form in the catalyst is not known. In order to bind the fluorine, it is necessary that the catalyst contain alumina as such. Such materials as silica gel, activated carbon, and like materials which do not bind the fluorine, are not equivalent.

20 Particularly excellent results are obtained when using the catalyst described in patent number 536,212 which issued January 22, 1957. It consists of at least 7 parts by weight of molybdenum calculated as MoO_3 in the form of oxide or sulfide with 100 parts by weight of an alumina carrier obtained by precipitation from an aluminum salt solution, while during preparation of the catalyst HF or a substance producing HF under the conditions of the catalyst, preparation is added in the form of a solution with a concentration of not more than 1% by weight (calculated on HF) in quantities of less than 1% by weight of fluorine by 100 parts by weight of alumina. This

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method of preparation affords a very favorable distribution or combination of the fluorine in the catalyst. As shown in said application, if the fluorine is incorporated in the form of a solution of normal concentration, a less desirable and selective catalyst is obtained.

While the described catalyst containing molybdenum, aluminum, and fluorine, combined as indicated, gives exceptionally good results and is preferred, a reasonable conversion to the desired oil without extensive cracking can be obtained with certain modifications of the catalyst as follows: the molybdenum may be in part or even completely substituted by other Group VI metals, i.e., chromium, tungsten, uranium, or by manganese or vanadium. In addition, such materials as nickel and cobalt may be added as promoters.

The described catalyst affords the desired selective conversion of normally solid paraffin wax into quality lubricating oil without excessive cracking to gases and other lighter products only if applied under suitable and rather limited conditions. It is found that in the present process, the presence of substantial amounts of added hydrogen is essential. Inert gases such as nitrogen or 20 gases containing olefins which would react with and use up the hydrogen are not equivalent and are not suitable. The preferred mole ratio of hydrogen to hydrocarbon feed is from 10:1 to 60:1. It is also essential that the hydrogen be employed under pressure. Thus, a pressure of 10 atmospheres is the absolute minimum and pressures of at least 20 atmospheres are to be recommended. On the other hand, it is found that the desired isomerization is severely reduced by pressure. It is, therefore, preferable that the pressure does not substantially exceed about 40 atmospheres, although pressures up to 50 atmospheres may be applied with somewhat lower conversions.

The temperature in the reaction zone must be between about 350°C and about 450°C and is preferably between 400°C and 440°C. Higher temperatures lead to a sharp rise in the cracking.

The process may be effected with the paraffin wax in the vapor phase, in which case sufficient hydrogen must be supplied to vaporize the wax. In general, isomerization proceeds most successfully when the process is carried out with the wax in the liquid phase, and especially when the molten wax and hydrogen are passed concurrently downward through the catalyst bed. Under the specified
10 conditions, a short contact time of less than 10 minutes, e.g., 0.5 to 6 minutes, or even less in some cases, gives a substantial and selective conversion. Thus, throughput rates of 1-5 kilograms of paraffin wax per liter of catalyst per hour are possible with conversions per pass of the order of 30-60% and selectivities around 90%.

EXAMPLE I

A paraffin wax fraction with an average molecular weight of 308 and melting at about 41°C was passed, in the vapor phase at the rate of 2.5 kg/litre of catalyst per hour, together with 52
20 moles of hydrogen per mole of paraffin wax, at 425°C at a pressure of 35 atm., over a catalyst composed of 11 parts by weight of MoO₃, 100 parts by weight of Al₂O₃, and 0.5 part by weight of fluorine, which was prepared as follows:

A solution of 966 gm of AlCl₃.6 aq in 10 litres of water was intensively mixed with 10 litres of a 2.7% ammonia solution. Mixing was effected by introducing each of the solutions tangentially into a mixing chamber at the rate of 20 litres per hour in such a manner that, after mixing the pH varied between 8 and 8.5. Aluminum hydroxide gel precipitated without heating. As soon as

precipitation was complete, the reaction mixture was heated to a temperature between 50°C and its boiling point. The slurry obtained was agitated for a quarter of an hour, filtered, and washed with 70 litres of 0.25% ammonia solution until the washing water after acidification with HNO_3 did not show any precipitation with AgNO_3 . Subsequently, the product was again washed with 10 litres of distilled water.

The filter cake was intimately mixed in the form of a paste with 100 ml of an HF-solution containing 1.0 gm fluorine. After 10 half an hour, 100 ml of ammonium molybdate solution containing 27 gm ammonium molybdate (81.4% MoO_3) was added while intensively stirring. The mass obtained was evaporated to dryness on a steam bath, further dried at 120°C and calcined for 2 hours at 500°C in a nitrogen atmosphere.

The product was broken into pieces of 3 to 6 mm, after which the catalyst was ready to use.

The catalyst contained 10% by weight of MoO_3 on alumina, and also 0.5% by weight of fluorine, or 11 parts by weight of MoO_3 per 100 parts by weight of Al_2O_3 .

20 Of the isomerized product obtained, 12.2% by weight boiled below 300°C, 38.9% by weight consisted of a paraffin wax melting at 41°C (obtained by cooling and filtration at -5°C) and 48.9% by weight was a filter oil solidifying at 5°C (this determination and also the following determinations of paraffin wax were made in a medium of 5 parts by weight of methyl ethyl ketone and 1 part by weight of paraffin wax fraction).

The original paraffin wax fraction boiled as a whole above 300°C and consisted for 93.8% by weight of a paraffin wax obtained by cooling and filtration at -5°C, having a melting point of 42°C, and 30 for 6.2% by weight of a filter oil.

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On further cooling of the filter oil obtained at -5°C to -20°C and filtration, 5.4% by weight of paraffin wax and 43.5% by weight of filter oil was produced, calculated on the original paraffin wax fraction. It was found that this filter oil had a pour point of -16°C , a viscosity index of 122, a viscosity at 100°F of 6.60 c.s. and at 210°F of 2.08 c.s.

The following table shows the results of a number of selected experimental liquid phase runs in which the molten wax and hydrogen were passed concurrently down through the catalyst
10 bed.

Isomerization of wax to oil

Feed Stock = Assam slab wax, average number of C atoms = 27
 Catalyst = $Al_2O_3-MoO_3-F$ (100-11-0.5 pts by wt)
 Type of Process = Liquid phase downflow

Run No. Catalyst hours	8-12 A		8-12 B		8-12 C		8-12 D		8-12 E		8-12 F		8-12 G		8-12 H		8-12 K		8-12 L		8-12 M		
	0-30	67-93	93-122	122-190	190-233	233-270	270-333	333-369	369-409	409-449	449-485	522-546	546-599										
<u>Operating conditions:</u>																							
Temperature - °C	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420	420
Pressure - atg.	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35
Space velocity - kg/litre.h	1.88	1.93	2.94	0.99	2.00	1.99	1.98	1.99	1.99	1.90	1.90	1.98	1.97	1.99	1.99	1.99	1.97	1.97	1.97	1.97	1.97	1.97	1.97
H ₂ /oil mole ratio	10.8	10.5	10.4	10.2	20.4	10.2	10.5	10.2	10.2	10.8	10.8	10.5	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.4	10.3	10.5	10.5
<u>Products - % wt on charge:</u>																							
Oil above 300°C ¹⁾	4.9	43.1	34.8	55.6	48.2	31.1	38.4	48.2	31.1	47.5	38.4	38.4	49.4	57.6	49.4	50.2	46.4	46.4	46.4	46.4	46.4	46.4	46.4
Cracked below 300°C	-	7.4	6.9	10.8	6.2	4.2	3.9	6.2	4.2	7.8	3.9	3.9	7.5	17.4	7.5	9.5	9.1	9.1	9.1	9.1	9.1	9.1	9.1
Conversion efficiency wax to oil - % ²⁾	-	84	85	86	87	86	85	87	86	85	85	90	86	75	86	83	82	82	82	82	82	82	84
<u>Oil Properties:</u>																							
Spec. gravity at 70/4°C	0.7758	0.7759	0.7762	0.7744	0.7773	0.7756	0.7756	0.7773	0.7756	0.7756	0.7781	0.7781	0.7755	0.7755	0.7765	0.7802	0.7794	0.7794	0.7794	0.7794	0.7794	0.7773	0.7773
Refractive index at 70°C	1.4325	1.4322	1.4328	1.4323	1.4338	1.4323	1.4331	1.4338	1.4323	1.4331	1.4336	1.4336	1.4323	1.4323	1.4332	1.4347	1.4347	1.4347	1.4347	1.4347	1.4347	1.4338	1.4338
Pour point - °C	11	11	11	8	11	14	11	11	14	8	11	11	5	5	11	11	8	8	8	8	8	11	11
Viscosity at 100°F - cs	11.22	11.31	11.40	11.07	12.27	11.41	11.30	12.27	11.41	11.30	11.99	11.99	10.54	10.54	11.43	11.94	11.89	11.89	11.89	11.89	11.89	12.15	12.15
Viscosity at 210°F - cs	3.07	3.08	3.11	3.03	3.21	3.19	3.09	3.21	3.19	3.09	3.21	3.21	2.86	2.86	3.09	3.17	3.18	3.18	3.18	3.18	3.18	3.26	3.26
Viscosity index	151	150	152	149	146	162	152	146	162	152	155	155	135	135	149	148	151	151	151	151	151	156	156
Activity check runs indicated by x		x					x			x					x							x	x

1) After dewaxing at -5°C of total liquid product above 300°C.

2) Conversion efficiency = oil produced x 100.
wax converted

The oils produced by the process of our invention are super oils for certain special purposes such, in particular, as lubricants for aircraft turbines. They not only possess unique viscosity properties but also are less volatile and more resistant to oxidation than other oils of equal viscosity. In other words, they combine lubricating properties and low volatility with extreme fluidity. Oils of this character are obtained from paraffin wax only by effecting the isomerization in the absence of appreciable cracking. Since the viscosity of the oil produced is largely a
10 function of the molecular weight of the oil and this is in turn substantially equivalent to that of the paraffin wax feed, the viscosity of the desired product may be adjusted from a low gravity light aircraft turbine oil, such as illustrated, to relatively heavy oils corresponding to S.A.E. grades 10-30 by choosing paraffin wax feeds of different molecular weights.

Under the described conditions, the wax may be isomerized with a high and selective conversion continuously for many hours without the necessity of regenerating the catalyst. Regeneration of the catalyst when it becomes necessary, may be accomplished in
20 the usual manner by controlled burning of the carbonaceous deposits and subsequent reduction of the catalyst with hydrogen.

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

1. Process for conversion of paraffin wax to lubricating oil which comprises melting a normally solid paraffin wax, passing the resulting liquid wax into contact with a catalyst comprising in combination molybdenum, alumina, and fluorine in which the molybdenum calculated as MoO_3 is present in an amount of at least 7 parts per 100 parts of alumina and which contains less than 5% fluorine at a temperature between 350°C and 450°C and under a pressure between 20 and 40 atmospheres for a time between 0.5 and 6 minutes in the presence of at least 10 to 60 moles of added hydrogen per mole of wax.
2. Process for the production of lubricating oil by the catalytic isomerization of paraffin wax according to claim 1 further characterized in that fluorine in said catalyst is combined fluorine in a concentration of about 0.5%.
3. Process for the production of lubricating oil by the catalytic isomerization of paraffin wax according to claim 1 further characterized in that the alumina in the catalyst is obtained by precipitation from an aluminum salt solution and wherein fluorine in a quantity from about 0.5 part to 1 part by weight has been incorporated through the use of a solution having a concentration of not more than 1% by weight calculated as HF.
4. Process according to claim 1 in which the molybdenum in the catalyst is in part substituted by a metal selected from the group consisting of chromium, tungsten, uranium, manganese, and vanadium.