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PRODUCTION OF LUBRICATING OILS

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This invention relates to a process for manufacturing synthetic lubricating oils. More particularly, the invention is directed to an efficient catalytic method for producing lubricating oils having the desirable properties of low pour point, high viscosity index, among others, from normal alpha mono-olefins having at least 8 carbon atoms in the presence of a crystalline aluminosilicate.

There are many catalysts which are known to polymerize alpha mono-olefins to lubricating oils. Among these are Friedel-Craft catalysts, such as $AlCl_3$, and free radical catalysts, such as di-tertiary-butyl peroxide. Both types decompose during the process and are eliminated, adding to the cost of the process. On the other hand, solid acidic oxide catalysts, such as silica alumina, do not decompose but during the polymerization reaction build up surface coke which can be subsequently removed by air oxidation. These known acidic oxide catalysts, however, provide an oil product which, in general, does not have sufficiently high viscosity indices and/or low pour points required of a satisfactory lubricating oil.

Accordingly, a method for manufacturing lubricating oils having high viscosity indices and low pour points has been discovered wherein a normal alpha mono-olefin having between 8 and 18 carbon atoms per molecule is heated at a temperature in the range from about 350° F. to about 590° F. in the presence of a crystalline aluminosilicate which has uniform pore openings in excess of 6 angstrom units and is substantially free of alkali metals. An outstanding advantage of this process is the realization that the crystalline aluminosilicate catalyst, used herein, can be regenerated and reused without loss of high viscosity index and/or low pour point of the resulting lubricating oil product.

The reactants for the production of synthetic oils in accordance with this invention are normally liquid, straight-chain 1-olefins ranging from 1-octene to 1-octadecene, including 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene and mixtures thereof. It must be clearly understood that by straight-chain 1-olefins is meant mono-olefins containing the double bond in the alpha position and having a normal structure. The most desirable synthetic lubricating oils are produced from straight-chain 1-olefins containing from 10 to 14 carbon atoms per molecule.

The state of purity of the straight-chain 1-olefin charge is only critical if the change is contaminated with substantial quantities of aromatic hydrocarbons or with oxygen-containing materials. This contaminated charge stock may produce a lubricating oil having inferior characteristics. However, since paraffins are not involved in this reaction, it has been found that charge stocks containing as much as 50 percent by weight of paraffinic hydrocarbons with the balance straight-chain 1-olefins having between 8 and 18 carbons atoms per molecule are entirely satisfactory for this process. In many instances, in commercial operation, it may be desirable to use technical grades of such olefins as 1-octene, 1-decene, and the like. The preferred charge stock is the relatively pure single olefins containing from 8 to 18 carbon atoms per molecule, although mixtures containing these olefins are satisfactory. The use of normal alpha mono-olefins having less than 7 and particularly less than 6 carbon atoms per molecule will not provide the lubricating oil having the desired physical properties.

The catalytic agents utilized in the process of the present invention are crystalline aluminosilicates which have uniform pore openings in excess of 6 angstrom units, preferably in the range from about 6 to about 15 angstrom units and are substantially free of alkali metals. The crystalline aluminosilicates used herein are frequently referred to as synthetic zeolites. These materials are essentially the dehydrated forms of crystalline hydrous siliceous zeolites containing varying quantities of various metals, other than alkali metals, and aluminum. The particular metal atoms, silicon, aluminum and oxygen in these zeolites are arranged in the form of an aluminosilicate salt in a definite and consistent crystalline pattern. The structure contains a large number of small cavities, interconnected by a number of still smaller holes or channels. These cavities and channels are precisely uniform in size.

The catalytic agents, utilized herein, can be prepared by base exchanging a crystalline alkali metal aluminosilicate which has a uniform pore opening in excess of 6 angstrom units with any ionizable compound of a metal capable of replacing the alkali metal. The alkali metal aluminosilicate can be prepared following the general procedure described in U.S. Patent 2,882,244, Belgian Patents 577,642 and 598,582, as well as other known procedures used to prepare a crystalline aluminosilicate.

In the base-exchange operation, ionizable compounds of metals will be used wherein the replacing ion is in the cationic state. Inorganic salts will usually be employed. Suitable materials include soluble compounds of calcium, magnesium, manganese, vanadium, chromium, cerium, aluminum, lanthanum, praseodymium, neodymium, samarium, and other rare earth ions, such as europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium, as well as solutions containing mixtures of these ions and mixtures with other ions, such as ammonium. If ammonium ions are used in the base exchange, the steaming effect, hereinafter described, will liberate the ammonia ions and permit the hydrogen ion to remain. Organic salts of the foregoing metals, such as acetate and formate may also be used, as well as very dilute or weak acids. The use of a hydrogen-containing solution to replace the alkali content with hydrogen can also provide an effective catalyst. While water will ordinarily be the solvent in the base-exchange solutions used, it is contemplated that other solvents, although generally less preferred, may be used. Thus, in addition to aqueous solutions, alcoholic solutions, etc., of suitable compounds as noted above, may be employed in producing the catalytic agent utilized in the present process. It will be understood that the compounds employed for the base-exchange solution undergo ionization in the particular solvent used.

The base exchange required for introducing the necessary replacing ions is carried out for a sufficient period of time to replace the alkali metal content to below about 2 weight percent, preferably below 1 weight percent and more preferably below 0.5 weight percent. If the alkali metal content, especially sodium, is above the 2 weight percent level, the yield of lubricating oil is drastically reduced to a level which is not economically feasible.

After the base-exchange operation has been completed, the catalytic agent is dried at temperatures of 200–650° F. The dried catalytic agent can then be subjected to a further treatment. Such treatment entails heating the dried catalytic agent in an atmosphere which does not adversely affect the catalyst; such as, steam, air, nitrogen, hydrogen, flue gas, helium or other inert gas. Generally, the dried material is heated in steam or steam-air mixture to a temperature in the approximate range of 500° F. to 1500° F. for a period of at least about one hour and usually between 1 and 48 hours.

The preferred catalysts in the process of this invention are a rare earth aluminosilicate and a combination of rare earth hydrogen aluminosilicate having uniform pore openings in the range from about 6 to 15 angstrom units and substantially free of alkali metal content. A more preferred catalyst is a steamed rare earth aluminosilicate, as described above, and containing an alkali content below about 1 weight percent and preferably, below about 0.5 weight percent of said catalyst.

The amount of catalyst used to prepare the desired lubricating oil product herein can vary from about minor amounts to about 80 weight percent of the olefin charge. It is preferred, however, to utilize about 6 to about 60 weight percent catalyst based on the olefin charge to provide acceptable yields of the lubricating products having the high viscosity index and low pour point properties.

The temperature of this process which produces satisfactory yields, i.e. yields in excess of about 5 percent by weight based on the starting material and preferably in excess of 10 weight percent, ranges from about 350° F. to about 590° F. The preferred temperatures range from about 400° F. to about 500° F. At temperatures below 350° F., the reaction is exceptionally slow and requires an extensive period of time to provide acceptable yields of the desired lubricating oil product. At the undesired temperatures in excess of 590° F., extensive cracking conditions are anticipated resulting in a substantial decrease of the viscosity index of the lubricating oil product.

The time of reaction varies with the temperature, olefin charge, catalyst concentration and catalyst which is used. Generally, the reaction period can range from about ½ hour, or lower, to 20 hours, or longer. Under the preferred conditions, a reaction of only ½ hour to 5 hours is required to obtain acceptable yields of the desired lubricating oil product.

Pressure to be used is not especially critical. Pressures from atmospheric to 1000 pounds per square inch gauge can be utilized, however, it is desired to utilize pressures as low as possible and, preferably, utilize atmospheric or autogenous pressures, or less than 100 pounds per square inch gauge, if the reaction is carried out in a closed system.

The products from the reaction of this process include a monomer fraction (i.e. unreacted starting materials), a dimer fraction having a boiling range not exceeding 650° F., the lubricating oil fraction boiling above 650° F. to about 1200° F., and coke. These products can be separated by a distillation step, preferably by vacuum distillation. The yields of the lubricating oil fraction should be in excess of at least 8 weight percent and, preferably, in excess of 10 weight percent of the olefin charge. In order for the lubricating oil fraction to be an acceptable product for purposes of this invention, its viscosity index should exceed about 105, preferably in excess of 110, and have a pour point below about +5° F. If desired, the lubricating oil fraction can be further treated, such as hydrogenation to reduce any unsaturation which may be present or hydrotreated to remove any impurities which may be present, or the like. The monomer fraction can be recovered and recycled to obtain additional lubricating oil products. The dimer boiling to 650° F. can be satisfactorily used as a jet fuel per se, if desired, or can be hydrogenated further to improve its efficiency as a jet fuel. The carbonaceous product or coke has no further value and must be removed.

During the reaction, the catalyst used will be contaminated with coke and in time reduce its activity and efficiency. When this occurs, the coke can be removed utilizing an ordinary regeneration process by exposing the catalyst to a regeneration atmosphere, such as oxygen, hydrogen, or the like, under controlled conditions and improve the catalyst's efficiency and activity for reuse.

The process of this invention can be conducted in any type of equipment suitable for polymerization reactions. The process may be operated batchwise or on a continuous basis. Thus, this process can be adapted to operations using a fixed bed of catalyst, a moving bed of catalyst wherein the olefin flow can be concurrent or countercurrent to the catalyst flow or a fluid bed of catalyst, if desired.

The following examples will serve to illustrate the process of the invention without limiting the same:

Example 1

The crystalline sodium aluminosilicate having uniform pore openings between 6 and 15 angstrom units used as a starting material to prepare rare earth aluminosilicate was prepared according to the procedure described in U.S. Patent 2,882,244. The sodium aluminosilicate was base exchanged using about 60 times its weight of an aqueous solution containing 2 weight percent ammonium chloride and 5 weight percent rare earth chlorides containing as its principal constituent cerium chloride, along with the chlorides of praseodymium, lanthanum, neodymium and samarium. The base exchange was conducted continuously for 12 hours at 180° F. After the base-exchange operation was completed, the rare earth aluminosilicate was washed free of chloride at 180° F. using water. The resulting product was oven dried at 230° F. for 20 hours and calcined for 10 hours at 1000° F. Following the calcination step, the catalyst was further steamed for 24 hours at 1200° F. at 15 pounds per square inch gauge using 100% steam. The resulting rare earth aluminosilicate product contained 25.5 weight percent rare earth oxides, 0.21 weight percent sodium and a small amount of hydrogen ions and had a surface area of 389 square meters per gram.

Example 2

A rare earth aluminosilicate having uniform pore openings in the range between 6 and 15 angstrom units was prepared in the identical manner as the catalyst of Example 1 with the exception that the base exchange was conducted without the use of ammonium chloride in the rare earth chloride aqueous solution. The resulting catalyst contained 28.8 weight percent rare earth oxide and 0.39 weight percent sodium.

Example 3

A rare earth aluminosilicate having uniform pore openings in the range between 6 and 15 angstrom units was prepared by base exchanging a sodium aluminosilicate known as Zeolite Y, as prepared in the manner prescribed in Belgian Patents 577,642 and 598,582, with an aqueous solution containing rare earth chloride and ammonium chloride in the same proportions and manner as used to prepare the catalyst of Example 1. The steaming step following calcination was eliminated.

Example 4

To demonstrate the effect of the catalysts described in Examples 1 through 3 on 1-decene utilizing various reaction conditions, the following general procedure was utilized. The catalyst (14–25 mesh) and 1-decene was charged to an autoclave. The autoclave was pressure tested at 1000 pounds per square inch gauge nitrogen and the pressure released, thereby removing excess oxgen. The heat was then applied and the autoclave rocked for a reaction period of 5 hours. The pressure of the autoclave during the reaction never exceeded 100 pounds per square inch gauge. The liquid product was distilled in a single plate column under 2–4 millimeters pressure to obtain the various fractions. The amount of reactants, reaction conditions, yields of products and physical properties of the lubricating oil fraction are described below in Table I.

TABLE I

Example No.	1	1	1	1	1	1	1	2	3
Catalyst:									
Weight percent of charge	12	12	12	12	12	6	25	28	12
Grams	21	21	21	21	21	21	50	21	21
1-decene, grams	175	175	175	175	175	350	200	175	175
Reaction Temperature, ° F	400	450	500	590	650	400	400	400	400
Recovery, weight percent	99	97	95	90	97	98	98	99	97
Yields, weight percent:									
Monomer fraction	51	43	48	30	48	69	22	34	77
Dimer fraction (to 650° F.)	33	37	29	46	29	16	45	48	5
Lubricating oil fraction (650° F.+)	12	14	14	13	18	11	27	15	13
Coke	3	3	4	1	2	2	4	2	2
Lubricating Oil Properties:									
Gravity, ° API	38.6	35.0	33.8	28.5	33.7	39.2	36.5	36.6	42.0
Bromine No.	39.0	39.0	33.8	23	20	39.0	33.4	37	---------
Kinematic Viscosity, cs.:									
At 100° F	20.21	25.34	26.84	36.79	24.17	16.14	30.72	24.55	7.37
At 210° F	4.20	4.77	4.88	5.77	4.41	3.64	5.31	4.63	2.18
Viscosity Index	130	122	117	108	101	127	117	119	110
Pour Point	<−65	<−70	<−70	<−65	<−65	<−70	<−70	<−65	<−65

Example 5

In a reaction vessel equipped with a suitable stirrer, 350 grams of 1-decene and 42 grams of the catalyst of Example 1 were placed. The reactants were heated to 340° F. for a period of 5 hours with stirring during which time a stream of nitrogen was passed over the surface of the liquid-catalyst mixture. After this period of time, the resulting product only contained a yield of 2 weight percent of a lubricating oil based on the 1-decene charge.

Example 6

To demonstrate the effectiveness of the catalyst of Example 1 (rare earth aluminosilicate), various reactions were performed utilizing the similar reaction conditions described in Example 4 for specified periods of time after which the catalyst was regenerated to remove the accumulated coke by heating the catalyst in a stream of nitrogen containing 2 weight percent oxygen at 750° F. for 3 to 5 hours then increasing the temperature to 900° F. for 15 to 19 hours. The catalyst was then used for further reaction. The results of the data of this operation are tabulated in Table II below:

TABLE II

Regenerations	0	1	2	3
Catalyst:				
Weight percent of charge	50	50	50	50
Grams	50	179	172	160
1-decene, grams	100	358	344	320
Reaction temperature, ° F	400	400	400	400
Time of Reaction, hours	5	1	½	5
Recovery, weight percent	100	98	98	100
Yield, weight percent:				
Monomer fraction	11	19	19	20
Dimer fraction (to 650° F.)	44	37	42	33
Lubricating oil fraction (650° F.)	40	36	30	40
Coke	5	6	7	7
Properties of Lubricating Oil Fraction:				
Gravity, ° API	35.2	---------	36.6	37.5
Bromine No.	11	---------	25	22
Kinematic Viscosity, cs.:				
At 100° F	34.99	---------	30.28	19.92
At 200° F	5.74	---------	5.20	4.04
Viscosity Index	115	---------	114	116
Pour Point	<−65	---------	<−65	<−80

Example 7

Various 1-olefins were reacted utilizing the catalyst of Example 1 under the similar reaction conditions of Example 4. The results of these experiments are tabulated in Table III below:

TABLE III

Catalyst:			
Weight percent of charge	12	6	12
Grams	21	20	19
1-olefin	1-decene	1-dodecene	1-tetradecene
Grams	175	336	158
Reaction temperature, ° F	400	400	400
Reaction time, hours	5	5	5
Recovery, weight percent	99	100	97
Yield, weight percent:			
Monomer fraction	51	89	86
Dimer fraction (to 650° F.)	33	---------	---------
Lubricating oil fraction (650° F.)	12	10	10
Coke	3	1	1
Properties of Lubricating Oil Fraction:			
Gravity, ° API	38.6	38.6	38.8
Bromine No.	39	24	---------
Kinematic Viscosity, cs.:			
At 100° F	26.21	24.27	20.52
At 210° F	4.20	5.20	4.51
Viscosity Index	130	155	153
Pour Point	<−65	+5	−10

Example 8

Twenty grams of rare earth aluminosilicate catalyst (Example 1) and 252 grams 1-hexene were charged to the one liter stainless steel rocking autoclave. The autoclave was pressure tested with nitrogen at 1,000 pounds per square inch gauge, the pressure released, and the contents heated at 400° F. for 3 hours. The pressure dropped from 500 to 300 pounds per square inch gauge during that time. After coooling to room temperature, the p.s.i.g. was 0. The contents of the bomb were filtered through paper to separate liquid from catalyst particles, and the liquid thus separated distilled in a 15 plate podbielniak column. Residue boiling above 517° F. was 11 grams, or 4.4 weight percent of the 1-hexene charged, and had the following properties:

Specific gravity	0.83
Kinematic viscosity at 100° F., cs.	7.73
Kinematic viscosity at 210° F., cs.	2.11
Viscosity index	73

This product does not have desirable characteristics required of a satisfactory lubricating oil.

Example 9

Twenty grams of rare earth aluminosilicate catalyst (Example 1) was charged to the one liter autoclave. The autoclave was pressure tested with 1,000 pounds per square inch gauge nitrogen, pressure released, autoclave chilled (Dry Ice) and 135 grams propylene charged from a lecture bottle. The contents were then heated at 400° F. for 3 hours, the pressure dropping from 800 to 735 pounds per square inch gauge during that period. The autoclave was cooled to room temperature, gas vented, and 26 grams yellow liquid having an API gravity of 53.6 recovered. This was fractionated in a spinning band column, approximately 25 plates. The material boiling above 577° F. (5 weight percent of propylene charge) had the following properties:

Kinematic viscosity, at 100° F., cs.	22.49
Kinematic viscosity, at 210° F., cs.	2.22
Viscosity index	<0

This product does not have desirable characteristics required of a satisfactory lubricating oil.

Example 10

Crystalline sodium aluminosilicate (12 weight percent of olefin charge) having uniform pore openings of 4 angstrom units and prepared in the manner described in U.S. Patent 2,882,243, was used as a catalyst for the reaction of 1-decene at reaction temperatures of 400° F. for 5 hours utilizing the procedure described in Example 4. The sodium content of this catalyst exceeded 3.5 weight percent of said catalyst. A yield of less than 1 weight percent of a lubricating oil fraction was obtained.

The crystalline sodium aluminosilicate was base-exchanged with rare earth chlorides following the identical procedure described in Example 1. This rare earth aluminosilicate having pore openings of 4 angstrom units used as a catalyst for 1-decene under the same conditions described above provided a yield of a lubricating oil fraction of less than 1 weight percent of the olefin charged.

Example 11

Crystalline calcium aluminosilicate (12 weight percent of olefin charge) having uniform pore openings of 5 angstrom units prepared in the manner described in U.S. Patent 2,882,243, was used as a catalyst for the reaction of 1-decene at reaction temperatures of 400° F. for 5 hours utilizing the procedure described in Example 4. The calcium content of this catalyst exceeded 3.5 weight percent of said catalyst. A yield of less than 1 weight percent of a lubricating oil fraction was obtained.

Example 12

Crystalline calcium aluminosolicate (12 weight percent of olefin charge) having uniform pore openings of 10 angstrom units and prepared in a manner described in U.S. Patent 2,882,244, was used as a catalyst for the reaction of 1-decene at reaction temperatures of 400° F. for 5 hours utilizing the procedure described in Example 4. The sodium content of this catalyst was 3.5 weight percent of said catalyst. A yield of less than 1 weight percent of a lubricating oil fraction was obtained.

Example 13

Crystalline sodium aluminosilicate (12 weight percent of olefin charge) having uniform pore openings between 6 and 15 angstrom units and prepared in the manner described in U.S. Patent 2,882,244 was used as a catalyst for the reaction of 1-decene at reaction temperatures of 400° F. for 5 hours utilizing the procedure described in Example 4. The sodium content of this catalyst exceeded 3.5 weight percent of said catalyst. A yield of less than 1 weight percent of a lubricating oil fraction was obtained.

It is to be understood that the foregoing description is merely illustrative of preferred embodiments of the invention of which many variations may be made by those skilled in the art within the scope of the following claims without departing from the spirit thereof.

What is claimed is:

1. A method for manufacturing lubricating oils having a high viscosity index and low pour points from a normal alpha mono-olefin having between 10 and 18 carbon atoms per molecule, which comprises heating said mono-olefin at a temperature in the range from about 350° F. to about 590° F. in the presence of a crystalline aluminosilicate which has uniform pore openings in excess of 6 angstrom units and has an alkali metal content below about 2 weight percent.

2. A method for manufacturing lubricating oils having a high viscosity index and low pour points from a normal alpha mono-olefin having between 10 and 18 carbon atoms per molecule, which comprises heating said mono-olefin at a temperature in the range from about 400° F. to about 500° F. in the presence of a crystalline aluminosilicate which has uniform pore openings in excess of 6 angstrom units and has an alkali metal content below about 2 weight percent.

3. A method for manufacturing lubricating oils having a high viscosity index and low pour points from a normal alpha mono-olefin having between 10 and 14 carbon atoms per molecule, which comprises heating said mono-olefin at a temperature in the range from about 400° F. to about 500° F. in the presence of a crystalline aluminosilicate which has uniform pore openings in excess of 6 angstrom units and has an alkali metal content below about 2 weight percent.

4. A method for manufacturing lubricating oils having a high viscosity index and low pour points from a normal alpha mono-olefin having between 10 and 18 carbon atoms molecule, which comprises heating said mono-olefin at a temperature in the range from about 350° F. to about 590° F. in the presence of a crystalline aluminosilicate which has uniform pore openings between 6 and 15 angstrom units and has an alkali metal content below about 2 weight percent.

5. A method for manufacturing lubricating oils having a high viscosity index and low pour points from a normal alpha mono-olefin having between 10 and 18 carbon atoms per molecule, which comprises heating said mono-olefin at a temperature in the range from about 400° F. to about 500° F. in the presence of a crystalline aluminosilicate which has uniform pore openings betwen 6 and 15 angstrom units and has an alkali metal content below about 2 weight percent.

6. A method for manufacturing lubricating oils having a high viscosity index and low pour points from a normal alpha mono-olefin having between 10 and 18 carbon atoms per molecule, which comprises heating said mono-olefin at temperatures in the range from about 350° F. to about 590° F. in the presence of crystalline rare earth hydrogen aluminosilicate which has uniform pore openings between 6 and 15 angstrom units and has an alkali metal content below about 2 weight percent.

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