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Index at Acceptance :—**Class 2(iii)**, B1d.

COMPLETE SPECIFICATION.

Synthetic Lubricants.

We, SOCONY-VACUUM OIL COMPANY, INCORPORATED, a corporation organized and existing under the laws of the State of New York, United States of America, of 26 Broadway, City of New York, County of New York, State of New York, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

This invention relates to the production of viscous oils having highly desirable characteristics from olefins. More particularly, it relates to the production of lubricating oils having relatively high viscosity indices and relatively low pour points from liquid straight-chained 1-olefins containing from six to twelve carbon atoms, inclusive, per molecule. The process according to the invention consists in heating said olefins in the absence of a catalyst to a temperature of between 500° F. and 800° F.

The reaction may need as much as thirty hours to complete.

Processes have been proposed hitherto for converting petroleum distillates containing a high percentage of light unsaturated hydrocarbons into high viscosity lubricating oils with or without heating in the presence of a catalyst.

In accordance with United States Letters Patent No. 2,111,831 to Batchelder et al, normally-gaseous olefins, such as ethylene, may be converted into high viscosity index lubricants in the absence of active catalysts, at temperatures of 500° F. to 750° F. The present invention, however, does not contemplate the use of normally gaseous olefins as starting materials, but instead contemplates the use of normally liquid olefins.

Polymerization and condensation reactions in general have long been accomplished by the use of either heat or catalysts or both. Prior to the present invention, however, it was not known that the higher straight-chained 1-olefins such as normal decene-1 could be polymerized or condensed by heat alone to form synthetic oils, or that commercially feasible yields of oils having an exceptional combination of properties could be obtained by subjecting straight-chained 1-olefins containing between six and twelve carbons per molecule to controlled, non-catalytic polymerization reaction conditions.

Pure straight-chained 1-olefins may be used in accordance with this invention, but for economic reasons, it is generally preferred to use mixed olefinic materials such as are derived from the cracking of paraffin wax or other paraffinic materials, or from the Fischer-Tropsch process.

The olefins will be normally liquid, straight-chained 1-olefins ranging from hexene-1 to dodecene-1, inclusive. It must be clearly understood that by straight-chained 1-olefins we mean olefins containing the double bond in the alpha position and having a normal structure. In accordance with this invention the most desirable synthetic oils are produced from straight-chained 1-olefins containing not less than eight nor more than eleven carbon atoms per molecule.

The state of purity of the straight-chained 1-olefin charge does not appear to be especially critical. Although it is desirable to have a starting material which contains as large a percentage of the above described 1-olefins as possible, it is permissible to have present lesser amounts of other olefins and even of other hydrocarbon materials. In general, the charge stock preferably should contain less than about 20% by weight of hydrocarbons other than straight-chained 1-olefins having six to twelve carbon atoms per molecule. However, in the practice of our invention we have found that charge stocks containing as much as 50% by weight of paraffinic hydrocarbons with the balance straight-chained 1-olefins having between six and twelve carbon atoms per molecule are entirely satisfactory for our purpose. In many instances, in commercial operation, it will be found desirable to use

technical grades of such olefins as octene-1 or decene-1. Mixed olefinic materials derived from the thermal cracking of wax or from the Fischer-Tropsch process constitute satisfactory charging stocks.

Instability of product and unsuitability for lubricating oil use are evidenced by a dark brown color and a tendency to deposit dark, insoluble materials on storage. The carbon residue test (Conradson or Ramsbottom) also becomes excessive.

Tests indicate that when relatively pure, single olefins are polymerized in the absence of a catalyst, they should preferably contain not less than seven nor more than eleven carbon atoms per molecule, although mixtures of olefins containing as few as six or as many as twelve carbon atoms per molecule are satisfactory.

In non-catalytic polymerization, the most critical reaction condition is temperature. The range of temperature that produces satisfactory, commercially feasible yields of high quality synthetic oil varies from about 600° F. to about 700° F. At temperatures between 500° F. and 600° F. the conversion takes place at a slower rate and is usually less complete. At temperatures greater than 700° F. side and secondary reactions begin to occur and increase in importance to such an extent that at temperatures above about 750° F. the process again becomes impracticable if the best quality products are required in respect of viscosity, pour point and freedom from secondary reaction products.

These side and secondary reactions are chiefly the following:

1. The volatile non-oily components of the reaction mixture become progressively more saturated, as indicated by a decrease in bromine addition number and, therefore, less suitable for recycling for further conversion;

2. Cracking begins, as evidenced by greater gas pressure and decrease in oil yields; and

3. Cyclization begins, as evidenced by some decline in viscosity index with accompanying increase in gravity and refractive index.

The pressure to be used is not especially critical. It will usually be around 200 to 1000 pounds per square inch or higher depending upon the vapor pressure of the olefin reactant. Increased pressure is desirable and, as expected, increases the oil yields. The use of pressures of 100 pounds per square inch or higher is within the scope of this invention, with pressures upwards of 500 pounds per square inch being preferred.

The time of reaction varies inversely with temperature. Good products and good yields have been produced with times as short as one hour or less and as long as thirty hours. Preferably, the time is in the neighbourhood of five to ten hours, at about 600° F. A range of time of from three to twenty hours at a temperature of about 600° F. to 650° F. may be considered to be preferred for straight-chain 1-olefins having eight to eleven carbon atoms per molecule.

Test data also indicate that reasonable yields of products of comparatively high viscosity index may be obtained at temperatures of 750° to 800° F. and times of several minutes. These conditions are not preferred, however, because the products have higher pour points, and the material that is not converted into oil is degraded into light fractions of a relatively low degree of unsaturation and are therefore undesirable as recycle stock. The viscosity index decreases sharply with prolonged exposure to these higher temperatures.

Further details and advantages of this invention may be understood from the following examples which have been set forth in table form below.

TABLE I.

THERMAL CONVERSION OF DECENE-1.

Run No.	Temp. °F.	Time Hrs.	Press. Gauge	Yield % Chg.	Visc. 210° F.	V.I.	Pour Pt.	Bromine No.	Spec. Gr.	Neut. No.	Refr. Index
1	400	9	150	1.78	37.92	76.4	—	20.8	0.8580	—	1.4568
2	510	10	300	6.43	40.79	146	—	22.6	0.8309	—	1.4595
3	610	10¼	300	48.6	44.92	143	−20	17.0	0.8333	0.3	1.4632
*4	600	10	600	43.2	43.67	149	−15	18.0	0.8343	0.5	1.4618
5	660	9½	500	31.4	44.88	135	−10	14.5	0.8378	0.4	1.4661
6	700	9½	800	40.0	42.54	130.9	−10	13.7	0.8438	0.4	1.4672
7	700	1	300	33.8	47.69	136.5	−20	15.6	0.8393	0.6	—
8	700	3	200	48.4	50.20	131.7	−30	15.0	0.8443	0.3	—
9	705	5	100	38.8	48.82	128.2	<−30	12.2	0.8488	0.1	—
10	708	9	850	18.2	43.21	95.0	—	—	—	—	—
11	750	(1)	300	36.6	44.34	133.7	15	—	0.8453	—	—
12	750	3	600	30.0	40.31	116.3	—	—	—	—	—
13	750	5	650	26.6	40.31	109	<−30	—	0.8778	—	—
14	745	9	1100	9.6	72.57	27.2	—	—	—	—	—
15	800	(2)	500	26.2	44.66	134.5	20	—	0.8478	—	—
16	800	(3)	350	25.7	43.27	142	—	—	—	—	—
17	800	(4)	—	25.6	43.73	130	−20	—	0.8514	—	—
18	850	(5)	850	13.5	41.73	112.5	—	—	—	—	—
19	850	(6)	2500	6.3	119.2	0	—	—	—	—	—

(All reactions conducted in an atmosphere of N_2 unless otherwise specified.)

* Run in atmosphere of air.

(1) Bomb discharged immediately after 1 hour reaction time.
(2) Bomb discharged immediately after reaching 800° F., 13 minutes required for draining.
(3) Bomb discharged immediately after reaching 800° F., 8 minutes required for draining.
(4) Bomb discharged immediately after 30 minute reaction at 800° F., 8 minutes required for draining.
(5) Bomb discharged immediately after reaching 850° F., 18 minutes required for draining.
(6) Bomb discharged immediately after 30 minute reaction at 850° F., 31 minutes required for draining.

TABLE II.

THERMAL CONVERSION OF OTHER OLEFINS.

Olefin	Temp.	Time	Press.	Yield	Visc.	V.I.	Pour Pt.	Bromine No.	Sp. Gr.	Neut. No.
Propylene ..	610	10	1500	5.9	30	—	<-30	62.8	0.7887	1.4
Propylene ..	650	10	2400	8.5	43.6	-85	-25	46.9	0.9705	1.3
Butene-1 ..	650	9	1600	3.0	37.98	35.8	<-30	28.9	0.8462	10
Isobutylene ..	650	10	2325	2.8	43.79	<0	—	44.7	0.8822	—
Pentene-2 ..	605	10	1725	2.5	30	—	<-30	85.8	0.7778	1.2
Hexene-1 ..	610	9.5	900	9.9	37.67	85.0	<-65	20.5	0.8294	0.1
2-ethyl-hexene-1	650	9	1150	1.5	34.04	51.7	<-30	51.7	—	1.95
Octene-2 ..	650	20	900	10.5	37.09	34.8	<-30	52.1	0.8607	1.0
C_3 polymer (*) ..	640	9	600	1.74	—	—	—	—	—	—
Octene-1 ..	600	28	1400	45.0	43.92	128.4	<-70	14.3	0.8338	0.1
Octene-1 ..	610	10	700	29.6	43.14	126.2	<-70	14.9	0.8413	0.2
Dodecene-1 ..	600	10	250	50.0	45.18	152.6	+25	16.2	0.8294	0.2
Dodecene-1 ..	710	5	250	61.4	43.34	150	+45	15.7	0.8348	0.2
Hexadecene-1 ..	660	11	200	54.8	50.47	146	+75	12.8	0.8368	0.3

(All reactions conducted in an atmosphere of N_2 unless otherwise specified.)

* Mainly mixed nonenes of branched structure.

The reactions summarized in Tables I and II were conducted in shaker-type pressure bombs, and the autogeneous pressure due to the heating of the olefin reactant was used. It is within the scope of this invention to perform the reaction or conversion either by a batch process or a continuous process, and to recycle unconverted olefin reactant or partially converted olefin for further conversion.

After reaction, low-boiling materials were in each case removed by distillation, leaving the synthetic oils of this invention as a residue.

In the tables the pressure is given in pounds per square inch, gauge pressure. The yield is given as weight per cent of the charge, although in each run there was some material lost in the process so that the actual efficiency of the process was somewhat higher than indicated. The viscosity given is that measured by a Saybolt Universal machine at 210° F.

Referring more particularly to Table I, it will be apparent that, although synthetic oils can be produced over a somewhat wider range of temperatures, the most desirable combination of high yields, high viscosity index, and low pour point occurs in the range of temperatures varying from about 600° F. to about 700° F. It will also be apparent that pressure above about 200 pounds per square inch is not a critical factor. However, as far as is known at present, pressures of around 500 to 1000 pounds per square inch appear preferable. Table I also illustrates the fact that consid rable latitude in time of reaction is permissible.

The tests set forth in Table II were performed for the purpose of determining the type of olefins utilizable in accordance with the present invention. Isobutylene, pentene-2, 2-ethyl hexene-1, octene-2 and C_3-polymer are examples of materials which are either branched chain, or which contain their double bonds in other than the alpha position. The yields from all of these products are very low and none of the products has a satisfactory combination of characteristics.

With octene-1, decene-1 and dodecene-1, greatly improved yields are obtained but with dodecene-1 the pour points are far too high for the products to be considered satisfactory for most purposes.

From the foregoing and as stated hereinbefore, it is believed that, by adjustment of the reaction conditions, usable products can be obtained by thermal polymerization from straight-chained 1-olefins or mixtures thereof, having not less than six nor more than twelve carbon atoms per molecule, and this is particularly true if the olefins contain not less than eight nor more than eleven carbon atoms per molecule.

An indication of the effect of temperature and reaction time upon the characteristics and yields of the products may be obtained by reference to the appended drawings, in which:

Figure 1 is a graphic representation of the effect of temperature and reaction time upon viscosity index; and

Figure 2 is a graphic representation of the effect of temperature and reaction time upon yield.

The data for Figures 1 and 2 was obtained by a series of tests made on decene-1. The yield at 700° F. and using a three hour reaction time was 48.4% weight per cent of the charge, and the product had a viscosity index of 131.7 and a pour point of − 30° F.

As will be apparent to those skilled in the art, the process of this invention may be accomplished by either batch or continuous process.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for converting straight chain normally liquid 1-olefins containing from 6 to 12 carbon atoms in the molecule into viscous oils, which process comprises heating the said olefins in the absence of a catalyst to a temperature of 500 to 800° F.

2. A process as claimed in Claim 1, wherein the temperature is maintained between 600 and 700° F.

3. A process as claimed in Claim 2, wherein the olefins selected as starting materials are those containing 8 to 11 carbon atoms.

4. A process as claimed in any one of the preceding claims, wherein the pressure in the reaction vessel is maintained between 100 to 1000 pounds/in^2.

5. A process as claimed in any one of the preceding claims, wherein the 1-olefins contain paraffinic hydrocarbons in amounts not greater than 50% of the mixture and preferably hydrocarbons other than straight-chain 1-olefins in amounts less than 20% thereof.

6. A process for converting straight-chain normally liquid 1-olefins substantially as described.

7. Viscous oils when produced from straight chain normally liquid 1-olefins by the process claimed in any one of the preceding claims.

Dated this 15th day of April, 1948.

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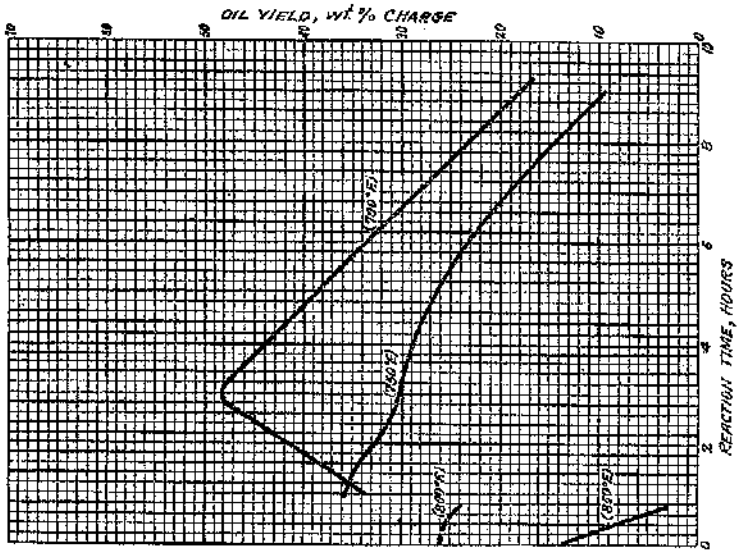

Fig. 2.

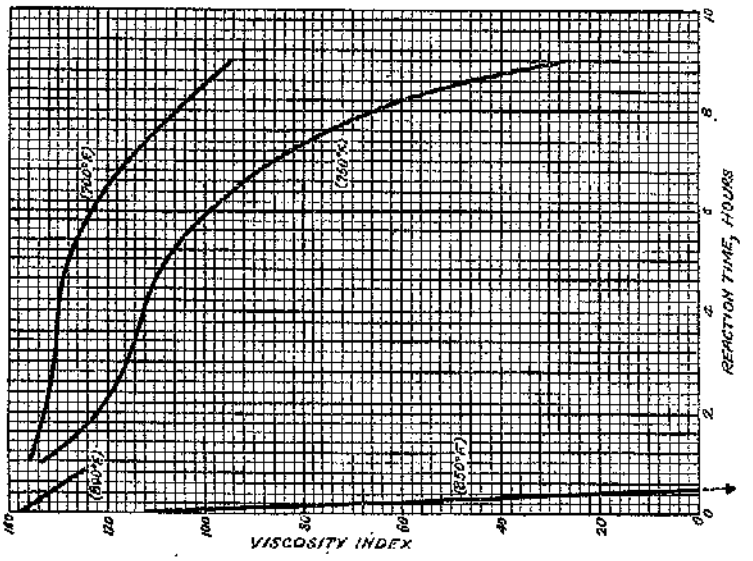

Fig. 1.

H.M.S.O. (M.F.P.)