Patented Mar. 14, 1950 2,500,165

UNITED STATES PATENT OFFICE

2,500,165

SYNTHETIC LUBRICANTS

Harry G. Doherty and Alexander N. Sachanen, Woodbury, and Francis M. Seger, Pitman, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

No Drawing. Application April 8, 1949, Serial No. 86,384

11 Claims. (Cl. 260—683.1)

1

This invention has to do with the production of synthetic lubricants and, more particularly, has to do with the production of these lubricants by a thermal, non-catalytic treatment of certain types of normally liquid olefins at high temperatures.

In a copending application, Serial No. 761,716, filed on July 17, 1947, abandoned in favor of application Serial No. 104,932, filed July 15, 1949, in which the inventors are two of those in the present application, a process has been described for the preparation of synthetic lubricants of excellent character, namely, high viscosity index, relatively low pour point and satisfactory stability. The process there described involves a thermal, non-catalytic conversion of normal, alpha mono-olefins having between about six and about twelve carbon atoms per molecule. Temperatures of operation range from about 500° F. to about 750° F., preferably from about 600° F. to about 700° F.

Although good yields of these desirable synthetic lubricants are obtained by so treating the aforesaid olefins at temperatures lower than about 700 F., the residence or reaction times required to produce commercially feasible yields is excessively long. As disclosed in the aforesaid copending application, however, yields of synthetic lubricants and the viscosity indices thereof diminish substantially as the temperature is raised above 700° F. and secondary reactions are initiated. Secondary reactions which are considered to be involved at the higher temperatures are:

(1) Degradation or cracking, as evidenced by decrease in oil yields;

(2) Cyclization begins, as evidenced by a decycle in viscosity index with accompanying increase in gravity and refractive index; and

(3) 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.

As a substantial improvement over the aforesaid process, it has now been discovered that synthetic lubricants possessing the combination of desirable properties referred to above, can be produced at temperatures greater than about 700° F. in good yields and in relatively short time periods. The present process comprises treatment of a normal, alpha mono-olefin having between about six and about fourteen carbon atoms per molecule, in the absence of catalytic material and in the presence of a minor and effective proportion of a paraffinic hydrocarbon, at temperatures greater than about 700° F. and not substantially above about 850° F. for relatively short reaction or residence times.

2

NORMAL, ALPHA MONO-OLEFINS

As indicated above, the mono-olefins of this invention are normal or straight chain alpha mono-olefins and contain between about six and about fourteen carbon atoms per molecule. Such mono-olefins are normally liquid at temperatures of the order of 20–25° C. Illustrative of such mono-olefins are the following: hexene-1, octene-1, decene-1, dodecene-1, tetradecene-1, and the like. Preferred, however, are those having from eight to twelve carbon atoms, with decene-1 representing a particularly desirable olefin. It will be clear from the foregoing examples than an alpha olefin may also be referred to as a 1-olefin.

Not only may the mono-olefins of the aforesaid character be used individually in this invention, but they may also be used in admixture with each other. In addition, olefin mixtures containing a substantial proportion of such mono-olefins may be used. Preferred of such mixtures are those containing a major proportion of a 1-olefin or of 1-olefins. In general, the charge stock preferably should contain less than about 20% by weight of unsaturated hydrocarbons other than straight chain 1-olefins. Representative of such mixtures are those obtained by the cracking of paraffin waxes and other paraffin products; those obtained from the Fischer-Tropsch and related processes.

These hydrocarbon mixtures may contain, in addition to the 1-olefin or 1-olefins, such materials as: other olefins, paraffins, naphthenes and aromatics.

In many instanoes, in commercial operation, it will be found desirable to use technical grades of 1-olefins. Mixed olefinic materials derived from thermal cracking of hydrocarbon wax or from the Fischer-Tropsch process constitute satisfactory charging stocks. In this connection, it must be noted that it is suspected that substantially straight chain 1-olefins, that is, 1-olefins in which the length of the side chain (or chains) is short relative to the length of the main chain, and in which the side chain (or chains) is not adjacent to the terminal double bond, are also suitable, although less advantageous charge stocks for the purpose of the present invention. In view of the unavailability of such olefins, however, no test data can be adduced to confirm this suspicion.

PARAFFINS

The paraffin hydrocarbons used herein to inhibit or retard secondary reactions may be normal or branched-chain in character, and contain about two or more carbon atoms. Typical of such paraffins are propane, n-butane, isobutane, n-pentane, n-heptane, isoctane, and the like. Hydrocarbon mixtures rich in such paraffins may also be used, in place of the individual paraffins. Representative of such mixtures are gasolines, propane-propene mixtures, and the like.

The chain length of the paraffin hydrocarbon is preferably varied with the temperature of operation. It has been found, for example, that the relatively short-chain paraffins, such as propane, butanes and pentanes, while effective at temperatures of the order of about 750°–850° F., are more advantageous at temperatures of about 850° F. The longer-chain paraffins are advantageous at temperatures from about 700° F. to about 750° F., their effectiveness decreasing with rising temperature.

With regard to the concentration of the paraffin inhibitor or retardant, minor amounts as low as about 0.1 per cent to about 50 per cent may be used. The proper amount of inhibitor or retardant will depend largely on the paraffin selected and the operating conditions. For example, pentanes have been found to be effective in concentrations from about 3% to about 50%, whereas paraffin wax is most advantageous in concentrations of one per cent or less due to its influence upon the pour point of the "residual" oil. Preferably, however, minor amounts of the order of about one to about 30% of the total charge are most effective.

REACTION CONDITIONS

The relatively high temperature and relative short reaction times of operation used in the present process, vary inversely with each other. When temperatures of the order of about 700–750° F. are used, reaction times are preferably from about three to about one hour; whereas, with temperatures of about 800° F., about one to about one-half hour reaction time is satisfactory. Operations at about 850° F. are attended by reaction times of about one-half hour to about one-quarter.

The operating temperatures and reaction times are critical features herein, as is the concentration of paraffin inhibitor previously discussed. The pressure to be used, however, is not particularly critical. It may range from about 100 to about 4,000 pounds per square inch, or even higher.

As indicated above, the present process is a thermal, non-catalytic process related to that described in said co-pending application Serial No. 761,716. The process is described as non-catalytic inasmuch as polymerization or condensation catalysts are not used. For example, Friedel-Crafts type catalysts such as aluminum chloride have hitherto been used to polymerize olefins, under conditions differing considerably from those recited above. It is with this in mind that the present process is described as "non-catalytic."

EXAMPLES

In order to illustrate the principles of this invention, the results of a series of typical, and non-limiting, conversions are set forth in tabular form in the several tables shown below. These conversions were carried out in rocking-type bombs (American Instrument Co.). The olefins and paraffin inhibitors were charged to the bombs. The bomb heads were secured and the bombs were flushed with nitrogen to displace air present therein. The bombs were then heated (while rocked) to the desired temperature for the desired length of time. Thereafter, the bombs were discharged either immediately by passing the hot reaction products through a condensing system, or after the reaction products had cooled to about 60–80° F. in the bomb.

It should be noted that the reaction times, recited as "Time, hours" in the tables, represent the time intervals during which the bombs were maintained at the desired temperature, and do not include the time intervals necessary to heat the bombs and their contents to the desired temperature, and do not include the time intervals necessary to cool the bombs after heat to the bombs has been discontinued. In general, about one and one-half hours are required to raise the temperature from 60–80° F. to 750° F., and about eight hours to cool thereafter to 60–80° F., in runs such as shown in the tables. However, since it has been shown in said copending application Serial No. 761,716 that substantially no polymerization occurs below 500° F., these times are of little significance. The experiments compared in the tables were made under directly comparable conditions.

The condensation products discharged from the bombs were vacuum topped to remove any unreacted hydrocarbon material and any relatively low boiling products and then were filtered, as in the runs shown in the tables. To distinguish the condensation products from the distillate fractions thereof, the refined oils are identified as "residual oils." The latter term identifies the oils from which unreacted materials and products of intermediate boiling range have been separated.

All of the tests and analyses to which the residual oils in the tables were subjected are well known standard tests. In this connection, it will be noted that the designation "N. N." refers to the neutralization number, which is a measure of the acidity of the oil.

In Table I below, several comparable runs are shown for conversions of 1-decene with and without n-pentane.

TABLE I

Conversions at 750° F. with and without n-pentane

Run No	1	2	3	4	5	6
Olefin Charged	1-decene	1-decene	1-decene	1-decene	1-decene	1-decene.
Parts by weight	740	740	400	740	700	388.
Inhibitor Charged	None	None	None	None	None	n-pentane.
Parts by weight						12.
Wt. per cent charge						3.
Reaction Time, Hrs	1	3	3	3	9	1.
Max. Pressure, p. s. i. g	300	600	700	650	1100	475.
Residual Oil:						
Yield, Wt. Per Cent Olefin Charged	36.6	30.0	32.8	26.6	9.6	45.1.
V. I.[1]	133.7	116.4	120.4	109	27.2	142.
Viscosity @ 160° F., Cs	29.87	21.86	21.16	22.42	242	26.67.
Viscosity @ 210° F., Cs	5.54	4.29	4.24	4.29	13.65	5.27.
Pour Point, °F	+15	+10	+15	<−30	−5	0.
Specific Gravity	0.8453	0.8639	0.8581	0.8778	0.9786	0.8373.
N. N	Nil	1.5		0.1	0.5	
Color (Lovibond)			100			3.7.
Carbon Residue (Ramsbottom)			0.06			0.01.

Run No	7	8	9	10	11	12
Olefin Charged	1-decene	1-decene	1-decene	1-decene	1-decene	1-decene.
Parts by weight	388	388	388	420	280	200.
Inhibitor Charged	n-pentane.	n-pentane.	n-pentane.	n-pentane.	n-pentane.	n-pentane.
Parts by weight	12	12	12	24	144	200.
Wt. per cent charge	3	3	3	5.4	34	50.
Reaction Time, Hrs	2	3	10	3	3	3.
Max. Pressure, p. s. i. g	100	500	1200	700	900	1200.
Residual Oil:						
Yield, Wt. Per Cent Olefin Charged	48.2	47.6	22.4	53.3	42.9	45.5.
V. I.[1]	139.1	142	109	133.8	145	148.
Viscosity @ 100° F., Cs	29.31	22.88	21.63	16.24	17.32	18.96.
Viscosity @ 210° F., Cs	5.59	4.71	4.20	3.71	3.95	4.21.
Pour Point, °F	+5	+15	−5	+15	+20	+10.
Specific Gravity	0.8388	0.8403	0.8735	0.8408	0.8324	0.8314.
N. N		Nil				0.2.
Color (Lovibond)	1.0	1.9	>750	4.5	0.35	1.0.
Carbon Residue (Ramsbottom)	0.03	0.02	0.3	Nil	0.01	Nil.

[1] V. I.'s above 140 are extrapolated values.

The results shown above in Table I demonstrate the appreciable improvement realized with an inhibitor, n-pentane, at 750° F. Runs 2–5 compared with runs 6–9 reveal the improvement obtained with n-pentane at different reaction times. By way of illustration, runs 1 and 6, 2–3 and 8 reveal a substantial improvement in yield and V. I. It appears that considerably better yields are obtained when the reaction time is from about one to about four hours; and that V. I. is relatively constant with a reaction time of less than about ten hours, and then diminishes. Runs 8–12 indicate the influence of inhibitor concentration; 5.4 per cent provides a somewhat higher yield than either 3, 34 or 50 per cent.

The series of runs set forth in Table II serve to indicate the influence of higher temperatures upon the conversion of 1-decene to synthetic lubricants.

TABLE II

Conversions at higher temperatures

Run No	1	2	3	4	5
Olefin Charged	1-decene	1-decene	1-dodecene	1-decene	1-dodecene.
Parts by weight	700	400	400	388	388.
Inhibitor Charged	None	None	None	n-pentane.	n-pentane.
Parts by weight				12	12.
Wt. per cent charge				3	3.
Reaction Temp., °F	850	852	852	850	850.
Reaction Time, Hrs	½	½	2	½	2.
Max. Pressure, p. s. i. g	2500	2000	1000		800.
Residual Oil:					
Yield, Wt. Per Cent Olefin Charged	6.3	4.7	14.0	12.4	17.8.
V. I.	Below Zero	Below Zero	59.6	78.3	106.6.
Viscosity @ 100° F., Cs	1738	195.6	108.3	27.25	26.22.
Viscosity @ 210° F., Cs	24.87	10.86	9.44	4.53	4.69.
Pour Point, °F	+45		−10	+10	+50.
Specific Gravity			0.9529	0.8973	0.8866.
N. N	0.8			0.6	
Color (Lovibond)			750	300	450.
Carbon Residue (Ramsbottom)		2.7	(1)	0.9	1.1.

[1] Value could not be obtained due to excessive foaming.

The results shown in Table II above, demonstrate the appreciable improvement in both yield and V. I. realized with an inhibitor, n-pentane, at 850° F.

Table III shows a series of runs made with and without another inhibitor, propane in the form of a propane-propene mixture.

TABLE III

Conversion at Various Temperatures with and without propane-propene mixture [1]

Run No.	1	2	3	4	5	6	7	8
Olefin Charged	1-decene	1-decene	1-decene	1-decene	1-decene	1-decene	1-decene	1-decene.
Parts by weight	740	400	400	700	400	700	388	388.
Inhibitor Charged	None	None	None	None	None	(1)	(1)	(1)
Parts by weight						125	15	12.
Wt. per cent charge						15.0	3.7	3.0.
Reaction Temperature, °F.	750	750	802	850	852	752	805	852.
Reaction Time, Hours	3	3	2	½	½	3	2	½.
Max. Pressure, p. s. i. g.	600	700	900	2500	200	800	400	500.
Residual Oil:								
Yield, Wt. Per Cent Olefin Charged	30.0	32.8	26.3	6.3	4.7	44.5	35.8	34.6.
V. I.	116.4	120.4	123.7	Below Zero	Below Zero	130	126.6	145.
Viscosity @ 100° F., Cs.	21.86	21.16	30.69	1738	195.6	21.61	23.44	15.27.
Viscosity @ 210° F., Cs.	4.29	4.24	5.43	24.87	10.86	4.39	4.59	3.66.
Pour Point, ° F	+10	+15	+10	+45		+15	+20	+15
Specific Gravity	0.8639	0.8581	0.8576			0.8504	0.8545	0.8299.
N. N	1.5		0.1	0.8				
Color (Lovibond)		100	14.5			18	42	0.75.
Carbon Residue (Ramsbottom)		0.06	0.04		2.7	0.0	0.08	N. 1.

[1] Commercial product containing propane and propene in about 50-50 concentration.

While substantial improvement in yield and V. I. is obtained with the propane inhibitor at 750–800° F., as shown by comparison of runs 1–3 and 6-7, the improvement realized at 850° F. is of an extremely high order: an improvement of several hundred per cent in yield and more than 145 V. I. units.

The effect of various paraffins is shown by the series of runs in Table IV.

From these results, it appears that a paraffin having from about three to about five carbon atoms per molecule provides optimum improvement in yield and V. I.

As pointed out hereinabove, there is no need for an inhibitor when a 1-olefin is treated at temperatures below about 700° F. This is demonstrated by the series of runs presented in Table V below.

TABLE IV

Conversions at 750° F. using various paraffins

Run No.	1	2	3	4	5	6	7
Olefin Charged	1-decene	1-decene	1-decene	1-decene	1-decene	1-decene	1-decene.
Parts by weight	740	400	560	388	388	286	396.
Inhibitor Charged	None	None	n-butane	n-pentane	n-heptane	Isooctane	Paraffin Wax.
Parts by weight			232	12	12	114	4.
Wt. per cent charge			29.2	3	3	28.5	1.0.
Reaction Time, Hours	3	3	3	3	3	4	3.
Max. Pressure, p. s. i. g.	600	700	700	500	620	850	700.
Residual Oil:							
Yield, Wt. Per Cent Olefin Charged	30.0	32.8	49.8	47.6	32.7	47.5	43.2.
V. I.	116.4	120.4	146 [1]	142 [1]	125	122	122.
Viscosity @ 100° F., Cs	21.86	21.16	17.71	22.88	26.48	12.53	15.97.
Viscosity @ 210° F., Cs	4.29	4.24	4.01	4.71	4.95	3.10	3.59.
Pour point, °F	+10	+15	+20	+15	+25	+10	+40.
Specific Gravity	0.8639	0.8581	0.8423	0.8403	0.8565	0.8438	0.8514.
N. N	1.5		Nil	Nil			0.4.
Color (Lovibond)		100	5	1.9	36	13	25.
Carbon Residue (Ramsbottom)		0.06	0.02	0.02	0.1	0.02	0.09.

[1] This value was extrapolated from V. I. Table.

Runs 3–7 in which an inhibitor was used, all show improvement over the blank runs 1 and 2.

TABLE V

Conversions at 650° F.—10 hrs. reaction time—various inhibitors

Run No.	1	2	3	4	5	6	7 [3]
Olefin Charged	1-decene	1-decene	1-decene	1-decene	1-decene	1-decene	1-decene.
Parts by weight	700	388	679	350	200	388	140.
Inhibitor Charged	None	(1)	n-pentane	n-pentane	n-pentane	Hexadecane	(1)
Parts by weight		12	21	36	200	12	130.
Wt. percent charge		3	3	9.3	50	3	48.
Residual Oil:							
Yield, Wt. Percent Olefin Charged	64.3	48.5	62.6	66.9	32.5	55.7	29.3.
V. I. [2]	142	139.2	140	150	142	139.6	150.
Viscosity @ 100° F., Cs	30.10	31.88	29.83	22.33	24.54	32	36.49.
Viscosity @ 210° F., Cs	5.79	5.97	5.70	4.74	4.97	6	7.14.
Pour Point, °F	−5	−35	+5	+5	−20	−10	+70.
Specific Gravity	0.8373	0.8356	0.8403	0.8348	0.8343	0.8373	0.8353.
N. N	Nil		0.1				0.3.
Color (Lovibond)	7.0	0.3	1.0	0.25	0.43	36	
Carbon Residue (Ramsbottom)	Nil	0.01	Nil	Nil	0.03	0.04	

[1] Commercial Product of about 50-50 mixtures of propane and propene.
[2] V. I.'s above 140 are extrapolated values.
[3] Actual temperature for this run 660° F., actual time 11 hours.

Comparison of runs 1 and 2 of Table V shows that propane is actually deleterious in substantially reducing the oil yield. This is also shown by a comparison of runs 1 and 3, 5, 6 and 7.

In addition to yield and V. I. improvements realized with the present process, lubricating oil output, based upon reactors of equal size, may be substantially increased. As will be readily recognized, this is a factor of major importance in commercial operations. Increase in oil output is accomplished by a substantial reduction in residence time. This relationship is shown by the results tabulated below in Table VI.

TABLE VI

Conversions with 1-decene

Reaction Temp., °F.	Residence Time, Hrs.	Inhibitor	Charge Rate,[2] Units of Wt. per hour	Oil Yield [3] Units of Wt. per hour	V. I.
600	10	None	0.10	0.0415	142
650	10	do	0.10	0.0645	145
650	10	n-pentane	0.10	0.0669	150
650	3	None	0.33	0.113	142.5
750	3	do	0.33	0.100	116.4
750	3	do	0.33	0.140	112.2
750	3	n-pentane	0.33	0.176	133.8
750	3	do	0.33	0.157	142
800	2	None	0.50	0.132	123.7
800	2	(1)	0.50	0.179	126.6
850	0.5	None	2.0	0.126	Below Zero
850	0.5	(1)	2.0	0.692	145

[1] Propane-Propene mixture; 50–50%.
[2] Obtained by dividing one unit weight of 1-decene charged by number of hours of reaction time.
[3] Obtained by multiplying weight of Residual Oil by units of weight per hour.

As will be evident from the data presented above in Tables I to VI, the condensation products of this invention are highly desirable lubricants per se. They are also of considerable value as blending agents for other lubricating oils. They impart desirable viscosity index (V. I.) and pour point characteristics to the oils in combination therewith, for, as indicated above, they have advantageous viscosity index and pour point properties. In short, the synthetic oils find utility in "upgrading" other lubricants. Typical oils with which the synthetic oils may be blended are mineral oils such as are normally used in internal combustion and turbine engines. When so blended, the synthetic oils may comprise the major proportion of the final blended oil, or may even comprise a minor proportion thereof.

One or more of the individual properties of the synthetic lubricants of this invention may be further improved by incorporating therewith a small, but effective amount, of an addition agent such as an antioxidant, a detergent, an extreme pressure agent, a foam suppressor, a viscosity index (V. I.) improver, etc. Antioxidants which may be used are well known in the art, and are generally characterized by phosphorus, sulfur, nitrogen, etc. content; representative of such materials is a phosphorus- and sulfur-containing reaction product of pinene and P_2S_5. Typical detergents which may be so used are metal salts of alkyl-substituted aromatic sulfonic or carboxylic acids, as illustrated by diwax benzene barium sulfonate and barium phenate, barium carboxylate of a wax-substituted phenol carboxylic acid. Extreme pressure agents are well known; illustrating such materials are numerous chlorine and/or sulfur containing compositions, one such material being a chlor-naphtha xanthate. Silicones, such as dimethyl silicone, may be used to illustrate foam suppressing compositions. Viscosity index improving agents which may be used are typified by polypropylenes, polyisobutylenes, polyacrylate esters, and the like.

Contemplated also as within the scope of this invention is a method of lubricating relatively moving surfaces by maintaining therebetween a film consisting of any of the aforesaid oils.

It is to be understood that the foregoing description and representative examples are non-limiting and serve to illustrate the invention, which is to be broadly construed in the light of the language of the appended claims.

We claim:

1. The method for preparing a viscous oil from a normal, alpha mono-olefin having from about six to about fourteen carbon atoms per molecule, which comprises: thermally and non-catalytically heating a hydrocarbon charge consisting essentially of said olefin in the presence of a minor and effective amount of a paraffin, at a temperature greater than about 700° F. for a period of time from about three hours to about one hour, and less than about 900° F. for a period of time from about one-half hour to about one-quarter hour.

2. The method for preparing a viscous oil from a normal, alpha mono-olefin having from about six to about fourteen carbon atoms per molecule, which comprises: thermally and non-catalytically heating a hydrocarbon charge consisting essentially of said olefin in the presence of a minor and effective amount of a paraffin, at a temperature greater than about 750° F. for a period of time from about three hours to about one hour, and less than about 850° F. for a period of time from about one-half hour to about one-quarter hour.

3. The method as defined by claim 1, wherein the normal, alpha mono-olefin contains from about eight to about twelve carbon atoms per molecule.

4. The method as defined by claim 1, wherein the normal, alpha mono-olefin is n-decene-1.

5. The method as defined by claim 1, wherein the paraffin contains from about three to about five carbon atoms per molecule.

6. The method as defined by claim 1, wherein the amount of paraffin is from about one per cent to about thirty per cent.

7. The method for preparing a viscous oil from n-decene-1, which comprises: thermally and non-catalytically heating a hydrocarbon charge consisting essentially of said olefin in the presence of about three per cent by weight of n-pen-

tane, at a temperature of about 750° F. for about two hours.

8. The method for preparing a viscous oil from n-decene-1, which comprises: thermally and non-catalytically heating a hydrocarbon charge consisting essentially of said olefin in the presence of about thirty per cent by weight of n-butane, at a temperature of about 750° F. for about three hours.

9. The method for preparing a viscous oil from n-decene-1, which comprises: thermally and non-catalytically heating a hydrocarbon charge consisting essentially of said olefin in the presence of about three per cent by weight of a propane-propene mixture, at a temperature of about 850° F. for about one-half hour.

10. The method for preparing a viscous oil from a normal, alpha mono-olefin having from about six to about fourteen carbon atoms per molecule, which comprises: thermally and non-catalytically heating a charge consisting essentially of hydrocarbons containing at least about 80 per cent of said normal, alpha mono-olefin, in the presence of a minor and effective amount of a paraffin, at a temperature greater than about 700° F. for a period of time from about three hours to about one hour, and less than about 900° F. for a period of time from about one-half hour to about one-quarter hour.

11. The method for preparing a viscous oil from a normal, alpha mono-olefin having from about six to about fourteen carbon atoms per molecule, which comprises: thermally and non-catalytically heating a hydrocarbon charge consisting essentially of said olefin in the presence of a minor and effective amount of a paraffin, at a temperature greater than about 700° F. for a period of time from about three hours to about one hour, and less than about 900° F. for a period of time from about one-half hour to about one-quarter hour, at the higher operating temperatures said paraffin having from about three to about five carbon atoms per molecule and at the lower operating temperatures said paraffin having longer carbon chain length.

HARRY G. DOHERTY.
ALEXANDER N. SACHANEN.
FRANCIS M. SEGER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,442,440	Scoville	June 1, 1948

OTHER REFERENCES

Egloff, The Reactions of Pure Hydrocarbons, published by Reinhold Pub. Corp. (1937), pages 360–368.

Tilichezev et al., Pro. Conference on Cracking, Eng. Trans. in 260—683, pages 1–4 pertinent.

Nemtzev et al., Jour. Gen. Chem., vol. VIII, pages 1314–24 (1938), Eng. Trans. in 260—683.15, pages 1–7 pertinent.

Certificate of Correction

Patent No. 2,500,165 March 14, 1950

HARRY G. DOHERTY ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 29, for "isoctane" read *isooctane*; columns 7 and 8, Table III, last line of the eighth column thereof, for "N.1." read *Nil*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 26th day of December, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.