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2,937,129

SYNTHETIC LUBRICANT

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This invention relates to synthetic lubricants. It is more particularly concerned with novel synthetic lubricants produced by polymerization of normal, alpha monoolefins in the presence of a certain class of catalyst.

As is well known to those familiar with the art, olefin polymers have been produced in the presence of various catalysts. It has been proposed to produce synthetic lubricants by polymerizing olefins in the presence of peroxides, such as benzoyl peroxide. It was found that the polymer product contained substantial amounts of structural elements of the catalyst chemically combined therein. Thus, for example, these polymers contained relatively large amounts of oxygen.

It has now been found that polyolefin synthetic lubricants of high quality can be produced that are free of structural elements of the catalyst. It has been discovered that novel high quality synthetic lubricants can be produced by polymerizing normal alpha monoolefins in the presence of a di-tertiary alkyl peroxide catalyst. The lubricants of this invention are characterized by low pour point and high V.I. They are valuable, for example, as lubricants for jet engines for high altitude aircraft. As pour point depressants and V.I. improvers are not required, there are no problems of pour point reversion and of sheer stability.

Accordingly, it is a broad object of this invention to provide novel synthetic lubricants. Another object is to provide polymerized olefin synthetic lubricants that are free of chemically combined structural elements of the catalyst. Still another object is to provide synthetic lubricants having controlled viscosity. A further object is to provide polymerized olefin synthetic lubricants that have high viscosity indices and relatively low pour points. A specific object is to provide a synthetic lubricant produced by polymerizing a normal alpha monoolefin in the presence of a di-tertiary alkyl peroxide catalyst. Other objects and advantages of the present invention will become apparent to those skilled in the art, from the following detailed description.

In general, the present invention provides novel synthetic lubricants that are produced by contacting in a reaction zone, at a temperature varying between about 100° C. and about 200° C., a normal alpha-monoolefin, having between about 5 and about 14 carbon atoms per molecule, inclusive, with a di-tertiary-alkyl peroxide catalyst in an amount varying between about 0.01 mole and about 0.3 mole per mole of said monoolefin; said synthetic lubricant being characterized by a high viscosity index, a relatively low pour point, and freedom from chemically-combined structural elements of the catalyst.

The olefins utilizable in the present invention are the normal alpha-monoolefinic hydrocarbons having between 5 and 14 carbon atoms, inclusive, per molecule and preferably between 7 and 12 carbon atoms. The olefins contemplated are those normal olefinic hydrocarbons having a double bond adjacent the terminal carbon atom, such as pentene-1. Non-limiting examples of such

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olefins are hexene-1, heptene-1, octene-1, decene-1, undecene-1, dodecene-1, and tetradecene-1. The monoolefinic hydrocarbon reactant can be obtained from any source known to the art, and it can be in the pure state or in admixture with other constituents not undesirable. It is also contemplated to use mixtures of two or more olefinic hydrocarbon reactants.

The catalyst used to produce the polymerized olefin synthetic lubricants of this invention are the di-tertiary-alkyl peroxides. These peroxides can be represented by the formula, ROOR', wherein R and R' are like, or dissimilar, tertiary alkyl radicals. In preferred practice the tertiary alkyl radicals are lower tertiary alkyl radicals. Non-limiting examples of the catalyst are di-tertiary-butyl peroxide, di-tertiary-amyl peroxide, and tertiary-butyl tertiary-amyl peroxide.

The amount of peroxide catalyst employed in the process of this invention is determinative of the viscosity of the polyolefin synthetic lubricant product. In general, the more viscous lubricants are obtained when larger amounts of catalyst are used. The amount of di-tertiary-alkyl peroxide catalyst employed will vary between about 0.01 and about 0.3 mole per mole of normal alpha-monoolefin reactant.

The di-tertiary-alkyl peroxide catalyst can be added to the olefin reactant in a single addition. It is preferred, however, to add the catalyst in two or more portions at intervals of several minutes to several hours. A feasible procedure is to add the catalyst gradually to the reaction mixture throughout the course of the reaction.

The temperature employed in the process of this invention is the activation temperature of the catalyst. The di-tertiary-alkyl peroxides are activated at temperatures varying between about 100° C. and about 200° C., depending upon the particular peroxide selected. The pressure employed depends upon the temperature used and upon the olefin reactant. Ordinarily, a pressure sufficient to maintain the reactants substantially in the liquid phase is sufficient. The time of reaction depends, of course, upon the temperature employed, the nature of the reactants, and to some extent the pressure. In general, the higher the reaction temperature, the shorter the reaction time required. The criterion used is the time required, at a given temperature, to effect condensation and to assure substantially complete utilization of the catalyst. In general, the time of reaction will vary between about one hour and about 6 hours.

The process can be operated batchwise, semi-continuously, or continuously. In commercial operation, a continuous process is the most feasible from the economic standpoint. Regardless of the type of operation, it is essential that the monoolefinic hydrocarbon reactant be intimately contacted with the peroxide catalyst. This may be effected in several ways and in apparatus which are well known in the art, e.g., by agitation.

At the temperatures required for the process of this invention, some of the di-tertiary-alkyl peroxide catalysts together with alcohol may tend to distill from the reaction zone. This material can be gathered in a suitable trap or receiver and recycled to the reaction zone. It is preferable, but not necessary, to wash the material with water to remove alcohol prior to recycling.

As has been mentioned hereinbefore, the product of this invention is a synthetic lubricant of outstanding properties. The lubricant has a viscosity index of about 125 and higher and a low pour point, generally -35° F. and lower. The product differs from polymers produced with other peroxides, in that it contains no structural elements of the peroxide catalyst and has a higher viscosity index. Thus, the polymers made with benzoyl peroxide contain

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in the order of 5 percent oxygen, whereas the products of this invention contain negligible amounts of oxygen. Thermally polymerized olefins, on the other hand, although they have high V.I., have high pour points.

As those skilled in the art will appreciate, the synthetic lubricant product can be recovered by conventional methods, including stripping unreacted olefin, vacuum distillation, and the like. The synthetic lubricant product is generally the residual matter after topping.

The following specific working examples are for the purpose of illustrating the synthetic lubricants of this invention and the manner of producing them. It will be understood that this invention is not to be limited to the specific olefins and catalyst used in the examples, or to the particular operations and manipulations involved. Other olefins and catalysts as defined hereinbefore can be used, as those skilled in the art will readily appreciate.

EXAMPLE 1

A mixture of 3100 grams (22.2 moles) of decene-1 and 32 grams (0.23 mole) of di-tertiary-butyl peroxide were heated in a reaction vessel, at a temperature of 150–160° C. for about two hours. The reaction product thus obtained was topped to remove unreacted decene-1 and the topped product was subjected to vacuum distillation to a temperature of 220° C. at 3 mm. mercury pressure. There was obtained an oily residue weighing 341 grams and having the following properties:

Gravity, ° API	37.2
K.V. at 210° F., cs.	8.65
K.V. at 100° F., cs.	49.86
Viscosity index	141
Pour point, ° F.	< -65
Bromine No.	12.2
Molecular weight	650
Oxygen, wt. percent	0.25

EXAMPLE 2

A mixture of 3100 grams (22.2 moles) of decene-1 and 160 grams (1.1 moles) of di-tertiary-butyl peroxide was heated at 150° C. for about two hours. As a result of the reaction, the temperature of the reaction mixture rose to about 158° C. and then subsided to 150° C. Then, maintaining a temperature of 150° C., 480 grams (3.3 moles) of di-tertiary-butyl peroxide were gradually added to the reaction mixture over a period of 4 hours. Throughout the reaction period some butanol and peroxide catalyst distilled from the reaction zone. This was collected and continuously recycled.

The reaction mixture was topped and then distilled to a pot temperature of 240° C. at 3 mm. mercury pressure. The residual product was an oily material weighing 2604 grams and had the following properties:

Gravity, ° API	34.4
K.V. at 210° F., cs.	33.20
K.V. at 100° F., cs.	324.9
Viscosity index	125
Pour point, ° F.	-35
Molecular weight	1350

EXAMPLE 3

Into a reaction vessel were placed 1000 grams (5.94 moles) of dodecene-1. This was heated to 150° C. and 174 grams (1.19 moles) of di-tertiary-butyl peroxide were added gradually over a period of 2½ hours. During this period of time, the pot temperature was 165–200° C. Then the temperature was dropped back to 147° C. and maintained for about one additional hour.

By that time, 175 cc. of distillate (butanol and peroxide) had distilled off and were collected. Water was added to the distillate and 20 cc. of insoluble liquid (di-tertiary-butyl peroxide) separated. This material was added back to the reaction mixture and heating was continued for another 2 hours. The reaction mixture was topped to a pot temperature of 235° C. at 2 mm. mer-

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cury pressure. A polymer oil weighing 923 grams was recovered as the residue. This lubricant had the following properties:

Gravity, ° API	34.4
K.V. at 210° F., cs.	37.47
K.V. at 100° F., cs.	354.2
Viscosity index	127
Pour point, ° F.	-35

EXAMPLE 4

A mixture of pure olefins consisting of 250 grams (2.23 mole) of octene-1, 250 grams (1.79 moles) of decene-1, 250 grams (1.49 moles) of dodecene-1, and 250 grams (1.28 moles) of tetradecene-1 was placed in a reaction vessel and heated to 154° C. Then, 198 grams (1.36 moles) of di-tertiary-butyl peroxide were added gradually during a period of about 2 hours. The temperature during this time was 138–173° C. The distillate material (peroxide and butanol) amounting to 370 cc. was recycled and heating continued for another hour. After this period of time, 340 cc. of distillate were collected and water-washed. The insoluble portion, 166 grams di-tertiary-butyl peroxide was returned to the reactor.

Heating was continued at 150–170° C. for an additional 2 hours. During this period, distillate material was continuously collected, water-washed, and recycled as aforescribed. The reaction product was then topped to a pot temperature of 235° C. at 4 mm. mercury pressure. The residue, an oily liquid, weighed 895 grams. It had the following properties:

Gravity, ° API	33.7
K.V. at 210° F., cs.	40.35
K.V. at 100° F., cs.	402.1
Viscosity index	125
Pour point, ° F.	-35

EXAMPLE 5

For comparison purposes, two runs were made. In one run, a synthetic lubricant was produced using the procedure of Example 1, except that the catalyst used was dibenzoyl peroxide. The properties of this product compared with those of the product of Example 1 are set forth in Table I.

The other run was a thermal polymerization of decene-1. This run was carried out at 650° F. for 10 hours. The properties of the lubricant are also set forth in Table I, for purposes of comparison.

Table I

	Dibenzoyl Peroxide	Di-tertiary-butyl Peroxide	Thermal
Specific Gravity	0.894	0.8453	0.8373
Pour Point, ° F.	< -65	< -65	-5
K.V. at 210° F., cs.	8.10	8.65	5.79
K.V. at 100° F., cs.	56.02	49.86	30.10
Viscosity index	121.4	141	142

From the examples, it will be apparent that the present invention provides valuable synthetic lubricants having high viscosity index and low pour point. That the polymer oils of this invention are different in kind will be apparent from Table I. The thermal polymer is less viscous and has a relatively high pour point, although the viscosity index is high. The polymer made with dibenzoyl peroxide, on the other hand, has about the same viscosity and a low pour point, but the viscosity index is much lower. It also contains substantial amount of oxygen, whereas the product made with di-tertiary-butyl peroxide does not. Also, the latter product has both a very high viscosity index and a very low pour point.

This application is a continuation-in-part of copending application Serial Number 327,449, filed December 22, 1952, now abandoned.

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Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. A synthetic lubricant that is produced by contacting in a reaction zone, at a temperature varying between about 100° C. and about 200° C., a normal alpha-monoolefin, having between about 5 and about 14 carbon atoms per molecule, inclusive, with a ditertiary-alkyl peroxide catalyst in an amount varying between about 0.01 mole and about 0.3 mole per mole of said monoolefin; said synthetic lubricant being characterized by a high viscosity index, a relatively low pour point, and freedom from chemically-combined structural elements of the catalyst.

2. A synthetic lubricant that is produced by contacting in a reaction zone, at a temperature varying between about 100° C. and about 200° C., decene-1 with di-tertiary-butyl peroxide catalyst in an amount varying between about 0.01 mole and about 0.3 mole per mole of said decene-1; said synthetic lubricant being characterized by a high viscosity index, a relatively low pour point, and

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freedom from chemically-combined structural elements of the catalyst.

3. A synthetic lubricant that is produced by contacting in a reaction zone, at a temperature varying between about 100° C. and about 200° C., dodecene-1 with di-tertiary-butyl peroxide catalyst in an amount varying between about 0.01 mole and about 0.3 mole per mole of said dodecene-1; said synthetic lubricant being characterized by a high viscosity index, a relatively low pour point, and freedom from chemically-combined structural elements of the catalyst.

4. A synthetic lubricant that is produced by contacting in a reaction zone, at a temperature varying between about 100° C. and about 200° C., a mixture of octene-1, decene-1, dodecene-1, and tetradecene-1 with di-tertiary-butyl peroxide catalyst in an amount varying between about 0.01 mole and about 0.3 mole per mole of said mixture; said synthetic lubricant being characterized by a high viscosity index, a relatively low pour point, and freedom from chemically-combined structural elements of the catalyst.

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