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SYNTHETIC LUBRICANT PRODUCT OF POLYMERIZATION OF A VINYL ETHER WITH AN OLEFIN

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This invention relates to a synthetic lubricant, and it is more particularly directed to the provision of a polymeric material having lubricant qualities which is prepared by the copolymerization of an olefin with a vinyl alkyl ether.

Synthetic lubricants, as prepared from one or more of a wide variety of organic compounds, are playing an ever-increasing role in the lubrication field. The polyolefins and other synthetic hydrocarbon materials constitute one of the more important classes of such lubricants and have, in the main, a good viscosity index, a fairly low pour point and a viscosity which adapts them for use in many synthetic hydrocarbon lubricants employed as crankcase lubricants in gasoline engines. Unfortunately, however, when using many hydrocarbon synthetic oils, unduly large amounts of solid materials deposit out on the piston walls and other surfaces of the engine which come into contact with the oil. This deficiency, which is shared by many non-hydrocarbon synthetic oils as well, is apparently attributable to a poor solubility by the oil for the monomeric materials which are formed on oxidation of the gasoline (largely prior to ignition) and are discharged past the piston into the crankcase during the compression stroke. If these pre-ignition oxidation products, referred to herein as "cool-flame monomers," are not quickly dispersed through solution in the oil they rapidly give rise to the formation of gums and other solid materials which deposit out on the engine surfaces in the form of varnishes and lacquers.

In many cases it is desired to blend different synthetic lubricants with one another and/or with natural hydrocarbon oils. A good many of the synthetic lubricants, especially the polyolefins and similar hydrocarbon materials, are not readily miscible with some non-hydrocarbon synthetic oils. Accordingly, it would be desirable if a synthetic lubricant were available which would retain the many desirable qualities of the polyolefin type of synthetic lubricants, yet which would also have improved solubility for the cool-flame monomers as well as the ability to be blended in all proportions with other types of synthetic or natural oils. It would also be desirable if such a synthetic material were to have a lower than normal pour point and a relatively low viscosity, whereby the oil would be adapted for use under winter driving conditions.

It is our discovery that synthetic oils having the desirable attributes referred to above can be prepared by polymerizing one or more olefin reactants with a vinyl alkyl ether, or a mixture of such ethers, in the presence of a polymerization catalyst. The polymeric products so obtained have excellent lubricant qualities and are especially well adapted to be used as crankcase lubricants in automotive engines, though they can also be used for other lubricating purposes as well.

In particular, the polymer compositions of the present invention have a pour point which often is as low as —40° F., viscosities in the motor oil range, and good temperature-viscosity characteristics. Further, these polymers have a good capacity for dissolving cool-flame monomers, and as a result the piston walls and other surfaces of gasoline engines are maintained in a cleaner condition than is possible with many other oils. These qualities make the lubricant compositions of the present invention well adapted to be used in passenger car and other gasoline engines operated under city driving conditions where the production of cool-flame monomer products normally reaches a peak. It should also be noted that the synthetic lubricants of the present invention have excellent miscibility with non-hydrocarbon synthetic oils as well as with hydrocarbon oils of synthetic or natural origin; accordingly, they make excellent blending agents.

The lubricant of the present invention is formed by bringing one or more terminally unsaturated olefins into reactive engagement with a vinyl alkyl ether, or mixture of such ethers, in the presence of a polymerization catalyst. The reaction is exothermic in character and goes forward at either atmospheric or superatmospheric pressures without the necessary application of external heat. Preferably, however, a temperature of from about 30 to 200° C. is maintained in the reaction zone during the period in which the polymerization reaction takes place. Thus, in the case where a catalyst of the free radical initiating type is employed, the rate of reaction does not reach practical levels unless the reaction mixture is heated to a temperature sufficient to effect dissociation of the catalyst employed. Accordingly, when using catalysts of this type, it is preferred to maintain a temperature within the range noted above, which is known to dissociate the catalyst. If desired, the reaction can be conducted in the presence of a suitable solvent as, for example, benzene, petroleum ether, hexane, heptane or the like, though the reaction will also go forward in the absence of a solvent provided the reactants are thoroughly mixed. The use of a solvent is recommended when employing ethylene or other normally gaseous olefinic reactant since it is otherwise difficult to maintain a sufficient concentration of the olefinic material in the ether. If desired, the reaction mixture can be maintained under elevated pressure during the reaction, and good results have been obtained with pressures varying from atmospheric to about 1500 p. s. i. g. The use of higher pressures should be avoided since the same tend to favor the formation of materials having a molecular weight which is undesirably high from the lubricant standpoint. Appreciable reaction occurs in periods as short as 10 to 20 minutes, though in the preferred practice of the invention, reaction periods of one or more hours are employed in order to obtain maximum product yields.

The olefins employed in forming the polymeric materials of this invention are those which contain from 2 to about 16 carbon atoms in the molecule, and which are unsaturated in the terminal position. Representative olefins of this class are ethylene, propylene, 1-butene, isobutene, 1-pentene, 3-methylbutene-1, 1-hexene, 3-methylpentene-1, 1-octene, 2-ethylhexene-1, 1-decene, 1-dodecene and 1-hexadecene. These olefins can be employed either singly or in any desired combination in preparing the polymeric materials. A preferred class of olefinic reactants is made up of ethylene, propylene, 1-butene and isobutene, with blends of ethylene with one or more of the other members of this group constituting a more preferred reactant of this class.

The vinyl alkyl ethers employed in forming the polymeric lubricating materials are those wherein the alkyl group is one which contains from about 1 to about 16 carbon atoms. Representative ethers falling in this class are vinyl methyl ether, vinyl ethyl ether, vinyl isopropyl ether, vinyl n-butyl ether, vinyl sec.butyl ether, vinyl

tert.butyl ether, vinyl n-pentyl ether, vinyl n-hexyl ether, vinyl n-octyl ether, vinyl 2-ethylhexyl ether, vinyl n-decyl ether, vinyl n-dodecyl ether and vinyl n-hexadecyl ether.

As indicated above, the reaction by which the present polymeric lubricants are formed goes forward in the presence of a polymerization catalyst. This catalyst may be one of the free radical initiator type or it may be a Friedel-Crafts catalyst. Among the former may be mentioned organic peroxides such as benzoyl peroxide, acetyl peroxide, tert.-butyl hydroperoxide, di-tert.butyl peroxide, di-tert.amyl peroxide and lauroyl peroxide, as well as hydrogen peroxide, alkali metal perborates, persulfates and even oxygen itself. Representative Friedel-Crafts catalysts are boron trifluoride, boron trifluoride etherate (a complex of boron trifluoride and diethyl ether), aluminum chloride, zinc chloride and ferric chloride. When ethylene is employed as the olefinic reactant, there preferably is employed a free radical initiator, whereas with the other olefinic reactants it is preferable to employ a catalyst of the Friedel-Crafts variety, though it is also possible to employ a catalyst of the latter variety when ethylene is the olefinic reactant.

As regards the relative proportions of the reactants and of the catalyst to be employed, good results are obtained with reaction mixtures containing about 0.05 to 1 mole of the vinyl alkyl ether reactant for each mole of olefin. Preferably, however, there is employed from about 0.1 to 0.5 mole of the ether for each mole of olefinic reactant. The catalyst is effective when present in conventional amounts, the same normally being from about 0.01 to 5 mole per cent, based on the total moles of reactants employed.

The polymeric lubricant of the present invention is normally recovered as the relatively non-volatile, or bottoms portion of the reaction product which is left on distilling off the more volatile portion of the reaction mixture, though other conventional separation methods can also be employed. The material so recovered is composed of a mixture of polymers, which mixture can be used as such, or the individual components thereof can be separated from one another and employed as lubricants. Generally speaking, the products of this invention boil at temperatures above about 150° C. at 5 mm. Hg. They are also characterized by an average molecular weight of from about 400 to 700.

The synthetic materials whose preparation has been described above can be employed as lubricants either alone or when blended with any desired base oil stock. Said stock can be a Pennsylvania or other paraffin base oil, a refined naphthenic base oil, or a synthetic hydrocarbon or non-hydrocarbon oil of lubricating viscosity. As synthetic oils there can be mentioned alkylated waxes and similar alkylated hydrocarbons of relatively high molecular weight, hydrogenated polymers of hydrocarbons, and the condensation products of chlorinated alkyl hydrocarbons with aryl compounds. Other suitable oils for blending with the present polymers are those which are obtained by the polymerization of lower molecular weight alkylene oxides such as propylene and/or ethylene oxide. Still other synthetic oils with which the present compounds are miscible are those which are obtained by etherification and/or esterification of the hydroxy groups in alkylene oxide polymers, as represented by the acetate of the 2-ethylhexanol-initiated polymer of propylene oxide. Another important class of synthetic oils comprises the high molecular weight esters as, for example, di(ethylhexyl) sebacate.

The lubricants of the present invention, whether employed alone or blended with other oils, may have incorporated therein one or more additives of the type which are conventionally employed in lubricating oils. Such additives include pour point depressants, oiliness agents, extreme pressure additives, anti-oxidants, corrosion-inhibiting agents, blooming agents, thickening agents, and compounds for still further enhancing the already good viscosity index qualities of the oil. Again, there can also be employed various detergents such as the polyvalent metal phenates, sulfonates, and the like, as well as the various non-ashing detergents such as sorbitan monooleate, pentaerythritol monooleate, polymethacrylate-methacrylamides, and the like.

The following examples illustrate the present invention in various of its embodiments. The parts given therein are on a weight basis.

Example I

In this operation, 113 parts of vinyl butyl ether were dissolved in 400 parts of benzene, and the resulting solution was then charged into a bomb type of reactor vessel along with 10 parts of di-tert.butyl peroxide as catalyst. Ethylene was then charged to the bomb under pressure until 150 parts had been added. The bomb was then closed and heated to 150° C., at which temperature it was maintained for 12 hours, the bomb being agitated during the entire heating period. During this reaction period, the pressure in the bomb varied from about 1100 p. s. i. g. to 450 p. s. i. g. The contents of the bomb were then removed and distilled in vacuo until a pot temperature of 165° C. at 6.6 mm. Hg was reached, leaving as bottoms 22.3 parts of the desired polymeric lubricant material. Analysis of this material disclosed it to have the following properties:

Viscosity at 210° F	cs.	16.86
Viscosity at 130° F	cs.	64.1
Viscosity at 100° F	cs.	418.5
Viscosity index		132
Molecular weight		530
Carbon	per cent	81.3
Hydrogen	do	13.7
Oxygen (by difference)	do	5.0

From the above analysis it is evident that the polymer contained approximately 31% of the ether component. The polymer is found to be well adapted for use as a crankcase lubricant in gasoline engines since relatively small amounts of varnish and lacquer deposits form on the piston walls and other surfaces of the engine during operation thereof.

Example II

In this operation, which was conducted in the same general fashion as that described in Example I above, 67 parts of vinyl butyl ether and 20 parts of di-tert.butyl peroxide were added to 400 parts of benzene in the reaction vessel. A mixture of 130 parts of ethylene and 120 parts of propylene was then charged under pressure, following which the reactor was closed and heated at 150° C. for 12 hours. During the reaction interval the pressure within the vessel varied from about 1100 to 400 p. s. i. g. The reaction product was then removed from the vessel and distilled in vacuo until a pot temperature of 200° C. at 1 mm. Hg was reached. There remained 220 parts of bottoms having the following properties:

Viscosity at 210° F	cs.	20.12
Viscosity at 130° F	cs.	96.5
Viscosity at 100° F	cs.	228.6
Viscosity index		108
Pour point	° F.	−30
Bromine No.		7
Carbon	per cent	83.5
Hydrogen	do	14.1
Oxygen (by difference)	do	2.4
Calculated vinyl butyl ether content	do	16
Molecular weight	do	540

This material was found to be more soluble in a synthetic polyglycol lubricant than was a corresponding polyolefin lubricant of similar molecular weight.

Example III

In this case the operation of Example II was repeated. Here, however, the reaction temperature was raised to 200° C. and the reaction interval was reduced to 4 hours. Under these conditions there were recovered 98 parts of bottoms boiling above 200° C. at 1 mm. Hg and having the following properties:

Viscosity at 210° F	cs.	14.44
Viscosity at 130° F	cs.	67.76
Viscosity at 100° F	cs.	156
Viscosity index		98
Pour point	° F.	−40
Molecular weight		580
Bromine No.		9
Carbon	per cent	83.8
Hydrogen	do	13.7
Oxygen (by difference)	do	3.5
Calculated vinyl butyl ether content	do	22

Example IV

In this operation vinyl butyl ether was mixed with isobutene in such amounts that the latter reactant made up approximately 88 mole per cent of the charge. This mixture was then added in incremental fashion to a bomb type of reactor vessel in which boron trifluoride etherate (made up of 1 mole of boron trifluoride and 1 mole of triethyl ether) was present in the amount of about 2 mole percent based on the total moles of reactants employed. With each addition of the olefin and ether reactants, the pressure in the bomb was raised to about 50 p. s. i. g., and the temperature went up to about 40–50° C., following which both temperature and pressure fell off until the next increment of the reactants was added. After a total reaction period of about 4 hours, the contents of the bomb were removed and distilled in vacuo until a pot temperature of 200° C. at 0.6 mm. Hg was reached. Analysis of the resulting bottoms, which comprised 16 weight per cent based on the amount of monomer materials charged, disclosed the same to have the following properties:

Viscosity at 210° F	cs.	48.0
Viscosity at 130° F	cs.	316.5
Viscosity at 100° F	cs.	911.5
Viscosity index		104
Carbon	per cent	74.52
Hydrogen	do	12.15
Oxygen (by difference)	do	13.33
Calculated content of vinyl butyl ether	do	83
Molecular weight		600

Example V

Four and five-tenths parts of aluminum chloride was slurried in 120 parts of n-heptane, and a mixture of 140 parts of pentene-1 and 75 parts of vinyl ethyl ether was added dropwise. The rate of addition was such as to maintain the temperature below 80° C. The mixture was then heated at 80° C. for two hours. Two hundred parts of oil was recovered having a viscosity of 18.0 cs. at 210° F. The viscosity index of this oil was 105 and the pour point −40° F.

Example VI

Three and five-tenths parts of aluminum chloride was slurried in 100 parts of n-heptane. A mixture of 168 parts of dodecene-1 and 15 parts of vinyl ethyl ether was added dropwise to the aluminum chloride suspension. Reaction was carried out as in the preceding experiment, and a yield of 160 parts of oil was recovered. This oil had a viscosity of 20.0 cs. at 210° F. and a viscosity index of 120.

Example VII

This experiment was carried out under conditions similar to those of the two preceding experiments except here the charge consisted of 14.0 parts of pentene-1 and 6.3 parts of vinyl octyl ether added to a slurry of 0.5 part of aluminum chloride in 15.0 grams of heptane. 15.0 grams of viscous oil was recovered.

We claim:

1. A lubricant composition comprising a reaction product obtained by reacting ethylene with vinyl butyl ether at a temperature of about 150° C. in the presence of a free radical initiating catalyst, said reactants being employed in the ratio of from about 0.1 to 0.5 mole of the ether per mole of ethylene, and distilling off from the resulting reaction mixture at least that portion thereof boiling below about 150° C. at 5 mm. Hg, leaving as residue the desired lubricant composition having an average molecular weight of from about 400 to 700.

2. A lubricant composition comprising a reaction product obtained by reacting ethylene with vinyl butyl ether at a temperature of about 150° C. in the presence of di-tert. butyl peroxide, said reactants being employed in the ratio of from about 0.1 to 0.5 mole of the ether per mole of ethylene, and distilling off from the resulting reaction mixture at least that portion thereof boiling below about 150° C. at 5 mm. Hg, leaving as residue the desired lubricant composition having an average molecular weight of from about 400 to 700.

3. A lubricant composition comprising the reaction product obtained by reacting 150 parts by weight of ethylene with 113 parts by weight of vinyl butyl ether at a temperature of about 150° C. in the presence of 10 parts by weight of di-tert. butyl peroxide and distilling off from the resulting reaction mixture that portion thereof boiling below about 165° C. at 6.6 mm. Hg pressure, leaving as the residue the desired lubricant composition having an average molcular weight in the range of from about 400 to 700.

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