Patented June 6, 1950 2,510,540

UNITED STATES PATENT OFFICE

2,510,540

SYNTHETIC LUBRICANT

Seaver A. Ballard, Orinda, Rupert C. Morris, Berkeley, and John L. Van Winkle, San Lorenzo, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application March 17, 1947, Serial No. 735,250

9 Claims. (Cl. 260—615)

1

The invention relates to the use of certain polymers and copolymers as superior synthetic lubricants, and is particularly concerned with the use of a class of polymeric epoxides for lubricating purposes.

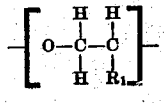
The use of mineral oil fractions for lubricating is suitable for many purposes, but it is well-known that such lubricants possess certain inherent limitations, such as tendency to oxidize, thickening at low temperatures, etc. A large number of additives have been employed with mineral oils in order to improve these shortcomings. To a certain degree, the resulting compositions may be used successfully for most lubricating purposes.

One of the important functions of a lubricant is the ability to maintain proper lubricating properties over a relatively wide range of operating temperatures. This feature of a lubricant, reflected in the viscosity of the lubricant at various temperatures, is of great importance, especially in aircraft lubricants, where hot ground temperatures as well as cold air temperatures are encountered regularly. Even if substances have other suitable lubricating properties, if their viscosity index is low their use as lubricants is apt to be extremely limited.

Polymers of propylene oxide also have been suggested as lubricants, and polymeric isobutylene oxide has likewise been employed. However, during recent investigations it has been found that isobutylene oxide polymers have very poor viscosity indexes, of the order of −130 to −250. Thus, even if these polymers have other suitable lubricating properties, this one inherent feature makes them unsuitable for use as lubricants. As an extension of the same investigation, it was found that 2,3-dimethylethylene oxide polymers also have very low viscosity indices making them unsuitable for lubricating purposes.

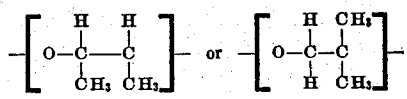
It is an object of this invention to provide a novel method of lubrication. It is another object of this invention to provide novel lubricating compositions. It is a third object of this invention to provide synthetic lubricants which may be combined with mineral oil lubricants in order to improve the latter. It is a further object of this invention to provide novel non-mineral oil lubricants. Other objects will become evident from the following disclosure.

Now in accordance with this invention, it has been found that lubricating compositions comprising polymers having units of the general configuration



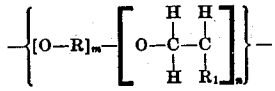
2

wherein R_1 is a hydrocarbon radical having at least two carbon atoms. This is especially surprising in view of the fact, mentioned hereinbefore, that polymers having units of either of these typical configurations



have such low viscosity indices that they are useless as lubricants.

Further, in accordance with this invention, it has been found that especially high viscosity index lubricants may be formed when using as a lubricant those copolymers having units of the general configuration



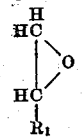
wherein m and n are integers, R is a hydrocarbon radical differing from that represented by R_1, and R_1 is a hydrocarbon radical having at least two carbon atoms likewise having high viscosity indices.

Still in accordance with this invention, it has been found that the polymeric and copolymeric lubricants of this invention are miscible with mineral oil lubricants and may be used therewith as lubricating compositions of improved properties.

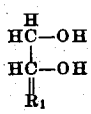
This solubility characteristic is unexpected, since polymers of a related epoxide, namely, propylene oxide, are insoluble in mineral oils.

Another unexpected feature of one phase of the present invention is the substantial lowering of the pour point of butadiene monoxide polymers upon hydrogenation. By this step the pour point may be lowered as much as 35° F. or more.

The polymeric lubricants may be made from alkylene oxides having the general configuration



or alkylene glycols having the general configuration



where, in either case, R_1 is a hydrocarbon radical having at least two carbon atoms. Preferably R_1 is a lower hydrocarbon radical, which is either

saturated or contains a double bond, having from two to twelve carbon atoms, and still more preferably from two to six.

Alkylene oxides having the above configuration include 1,2-epoxybutane, 1,2-epoxypentane, 1,2-epoxyhexane, 1,2-epoxyheptane, 1,2-epoxyoctane, 1,2-epoxynonane, 1,2-epoxydecane, 1,2-epoxydodecane, etc. As noted above, the hydrocarbon radical R_1 may be either saturated or unsaturated. Epoxides of the latter type include 1,2-epoxy-3-butene, 1,2-epoxy-3-pentene, 1,2-epoxy-3-hexene, 1,2-epoxy-3-heptene, 1,2-epoxy-3-octene, 1,2-epoxy-3-nonene, 1,2-epoxy-4-pentene, 1,2-epoxy-4-hexene, 1,2-epoxy-4-heptene, 1,2-epoxy-4-octene, 1,2-epoxy-5-hexene, 1,2-epoxy-5-heptene, 1,2-epoxy-6-heptene, 1,2-epoxy-7-octene, etc.

The corresponding glycols from which satisfactory polymeric lubricants may be prepared include saturated glycols such as 1,2-dihydroxybutane, 1,2-dihydroxypentane, 1,2-dihydroxyhexane, 1,2-dihydroxyheptane, 1,2-dihydroxyoctane, 1,2-dihydroxynonane, 1,2-dihydroxydecane, 1,2-dihydroxydodecane, etc. Unsaturated glycols which may be used in the preparation of these polymeric lubricants are 1,2-dihydroxy-3-butene, 1,2-dihydroxy-3-pentene, 1,2-dihydroxy-3-hexene, 1,2-dihydroxy-3-heptene, 1,2-dihydroxy-3-octene, 1,2-dihydroxy-3-nonene, 1,2-dihydroxy-3-decene, 1,2-dihydroxy-3-dodecene, 1,2-dihydroxy-4-pentene, 1,2-dihydroxy-4-hexene, 1,2-dihydroxy-4-heptene, 1,2-dihydroxy-4-octene, 1,2-dihydroxy-5-hexene, 1,2-dihydroxy-5-heptene, 1,2-dihydroxy-6-heptene, 1,2-dihydroxy-6-octene, 1,2-dihydroxy-7-octene, 1,2-dihydroxy-8-nonene, etc.

Preferred configurations are those in which the hydrocarbon radical, R_1 of the general formula, is an unbranched chain radical, or one having one short side chain attached thereto.

As noted hereinbefore, it has been found according to this invention that when these preferred classes of alkylene oxides and glycols are copolymerized with other alkylene oxides or glycols, the resulting copolymeric lubricants have high viscosity indices. The copolymers of the alkylene oxides may be prepared by copolymerizing one or more of the above alkylene oxide with one or more alkylene oxides of differing structure, such as propylene oxide, epichlorohydrin, 2,3-epoxy-4-ethoxybutane, 2,3-epoxy-5-hydroxypentane, 1,2-epoxy-3-dimethylaminopropane, etc.

When polymerizing epoxide derivatives the preferred catalyst is boron trifluoride, usually employed, as shown in the examples given hereinafter, as a complex with ether, which is gradually added to the polymerization mixture. Another preferred catalyst is aluminum chloride. The above catalysts are preferred because of their relatively great activity and the consequent low temperatures at which they may be used.

Other catalysts which may be used in the preparation of the subject polymeric lubricants include mineral acids, such as concentrated sulfuric acid, halogen acids, especially hydrogen iodide, heavy metal salts such as stannic chloride, sulfonic acids such as para-toluene-sulfonic acid, and basic substances such as sodium and potassium hydroxides.

The catalysts may be employed in solid, liquid or gaseous form, or may be present as an aqueous or organic solution. Hydrogen iodide, for example, is conveniently utilized in the present process as a concentrated aqueous solution, initially containing about 50% water. Others, such as the sulfonic acids, may be added as solids, liquids, or in either organic or aqueous solutions.

Dependent upon the nature of the monomer, the identity of the catalyst, the temperature of the polymerization reaction and the polymerization rate desired, the catalyst may be used in ratios with the monomer varying from about 1:500 to 1:10. Preferably, however, the ratio of catalyst is confined to the range from about 1:200 to 1:25, but a ratio of 1:100 gives satisfactory results in most circumstances.

The polymerization reaction may take place in either liquid, solution, emulsion or gaseous phases. Hence, the use of either liquid or gaseous diluents is contemplated. Liquid diluents may perform several functions by their presence, acting as solvents for the monomer and/or the polymer, as solvents for the catalyst, as azeotropic constituents for carrying off water formed during the polymerization, as diluents for the control of polymerization rate, or, by their boiling points, as controls for the temperature of the reaction, as one phase of an emulsified reaction mixture, etc. Gaseous diluents are used primarily when the polymerization is carried out in gaseous phase, but also may be injected to carry off the water formed during polymerization, or as coolants, etc.

Both gaseous and liquid diluents are preferably substantially inert toward the other components of the reaction mixture in the temperature range encountered prior to, during and after reaction. The most satisfactory diluents are hydrocarbons of either aromatic or aliphatic character, but preferably are saturated aliphatic hydrocarbons. When the diluent is to be used in an aqueous phase polymerization, it is preferably chosen from the group of hydrocarbons boiling between about 125° C. to about 300° C., especially if it is expected to participate in azeotropic distillation of water during polymerization. Hydrocarbons which serve as suitable diluents include the dihydronaphthalenes; cycloheptane, the decanes, including 2-methyl nonane and 2,6-dimethyloctane; the octanes, including 2,2,3-trimethylpentane and 2-methyl-3-ethylpentane; the nonanes, such as 2-methyloctane, 2,4-dimethylheptane, 4-ethylheptane, the dodecanes, such as dihexyl or 2,4,5,7-tetramethyloctane, etc.

When the polymerization is carried out in gaseous phase, the diluent may be a lower hydrocarbon such as methane, ethane, propane, butane, etc. which acts as a regulator or diluent for the reaction, but which can be stripped from the product with facility, subsequent to the polymerization.

The proportion of diluent is not a critical factor in carrying out the process of the present invention. However, it is a preferred practice to keep the reaction mixture as concentrated as possible, consistent with maintaining homogeneity, rate of polymerization, etc. Ordinarily, when a diluent is used for a liquid phase polymerization the initial proportion of diluent to monomer is from about 1:1 to about 20:1, but preferably is initially from about 2:1 to about 5:1. When the temperature of the reaction is substantially below the boiling point of the diluent, this ratio will remain unchanged throughout the reaction if, however, the conditions are such that water formed during polymerization distills azeotropically with part of the diluent passing over in the azeotrope may be replaced in or near the polymerization zone, so as to maintain a substantially constant diluent; glycol ratio.

Other ingredients may be included in the polymerization mixture, or may be added from time to time during the polymerization. For example, the polymerization may be carried out in a closed system such as an autoclave. In such a case, the water formed during the polymerization may be effectively removed by the presence of dehydrating agents which will combine with or absorb the water as it is formed. Inert gases such as nitrogen may be added to protect the hot polymerization mass from oxidation. Reactants, such as alcohols, may be present for the purpose of converting the hydroxyls normally present on both ends of the polymer chains to other functional groups, as more particularly set forth hereinafter.

The temperature when polymerizing glycol derivatives may vary considerably, but unless the reaction mixture is substantially above about 150° C. only a negligible amount of polymerization occurs, at least within a reasonable reaction period. If the reaction temperature is substantially above about 300° C., decomposition of the monomeric glycols and the polymers takes place to such an extent that undue losses occur and the product requires extensive purification. The preferred polymerization temperature range is from about 70 to 225° C., with the optimum range being from about 175 to about 200° C. Therefore it is a preferred practice to conduct the polymerization at temperatures somewhat below the point at which the glycols, thioethers or polysulfides will commence distilling, but, if higher temperatures are employed, the apparatus may be arranged so as as return the distilled glycols to or near the polymerization zone.

The polymerization of alkylene oxide derivatives may take place at temperatures from about 25° C. to about 175° C., but preferably is conducted within the range of 35° C. to 150° C. When using active catalysts such as boron trifluoride or aluminum chloride, relatively low temperatures are preferable so that the reaction rate may be conveniently controlled and copolymers of any desired molecular weight may be obtained.

When the polymerization is carried out by assembling all of the reactants in a vessel and heating with continuous or intermittent distillation of water, the reaction time required to obtain products having molecular weights of about 200 or more is at least about 2 hours, and usually is about 20 hours or even longer. Under a given set of conditions the molecular weight of the polymer varies directly with the amount of water formed. Consequently, the average molecular weight of the polymeric product can be readily calculated by the amount of water which has distilled out of the polymerization zone.

Following the polymerization period, the product is purified. The first step in purification is removal of catalyst. If this is a solid, suspended in the liquid polymer or a solution of the polymer, a simple filtration is all that is required. When the catalyst is in solution other means must be employed. For example, when sulfonic acids are the catalysts used, a preferred means for their removal from the polymer comprises dissolving or thinning the polymer with an organic solvent such as benzene, washing with concentrated caustic to convert the acid to the sodium salt, and subsequently extracting with water to remove the sodium salts of the acids and any remaining traces of caustic.

After removal of the catalyst, the product is dehydrated in order to remove the last traces of water formed during polymerization and any

water remaining from catalyst extraction operations. Water may be removed by the use of dehydrating agents, or by distillation, preferably under diminished pressure. If this latter method is employed, any solvents present and any monomers may be removed at the same time. Consequently, at the end of these operations there remains the copolymers free including solvents, water and catalyst.

The product may be decolorized if desired by treatment with bleaching agents, percolation through activated clays such as fuller's earth, hydrogenation, etc. The preferred treatment is a combination of percolation through fuller's earth followed by hydrogenation.

The percolation is preferably carried out at room temperature or below, but may be conducted at elevated temperatures, as long as the temperature and pressure adjustments are such as to prevent boiling of the solvent and consequent deposition of the copolymer in the percolation tower. This percolation treatment results in the production of copolymers having improved colors satisfactory for many purposes, in which case all that remains to be done is to flash off the solvent in order to recover the copolymer.

On the other hand polymers having the least color can be obtained only by following the persolation with hydrogenation. Neither persolation alone, or hydrogenation alone, or any of the ordinary decolorizing or bleaching procedures results in the formation of light colored copolymers such as those obtained by treatment with fuller's earth followed by hydrogenation.

In carrying out the percolation through fuller's earth, oxygen-containing solvents such as acetone, methyl alcohol, and dioxane are relatively ineffective for aiding in the removal of color from the subject copolymers. The color removal appears to be specific in that hydrocarbon solvents, and especially aromatic hydrocarbon solvents are required, benzene and toluene giving the best results.

The hydrogenation step is essential for the reduction of color-sensitive functional groups, supposedly carbonylic in character. Raney nickel, nickel sulfide, copper, palladium, platinum and other catalysts suitable for the reduction of carbonyls may be used, although Raney nickel is preferred. Temperatures employed vary from about 125 to about 250° C., and hydrogen pressures from about 500 to about 3000 lbs. per square inch are utilized. Subsequent to hydrogenation the catalyst may be removed from the product by super-centrifuging or filtration, and any solvents present are flashed off to yield the light yellow copolymer.

The polymers formed as described hereinbefore have hydroxyl groups on one or both ends of each copolymer chain. These hydroxyls may be acted upon with such materials as etherifying or esterifying agents in order to obtain products having altered properties, such as solubility or improved action as lubricants, plasticizers, etc.

Various etherifying agents may be used for etherifying terminal hydroxyls. These include alkyl halides, such as methyl iodide, methyl bromide, ethyl chloride, propyl iodide; aralkyl halides such as benzyl chloride and methylbenzyl chloride; hydroxyalkyl chlorides such as hydroxyethyl chloride; carboxyalkylating agents such as sodium monochloracetate; and alkylene halides such as allyl chloride. Ordinarily, the etherification is carried out in strongly basic environments; sodium hydroxide, liquid ammonia and

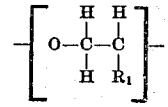
quaternary ammonium bases and salts being the usual basic substances present.

Esterification of the terminal hydroxyls may be accomplished with various inorganic groups such as nitrates, phosphates or sulfates. However, preferred esterifying agents are the organic acids anhydrides or acid chlorides, and especially fatty acid anhydrides and their chlorides, including for example, formic, acetic, propionic, butyric, hexoic, 2-ethylhexoic, and higher fatty acids such as lauric, stearic, myristic, palmitic and capric acids. Usually, the esters are formed by treatment of the hydroxylated polymer with the anhydride of the acid in the presence of a catalyst such as sulfuric or phosphoric acid. The saturated fatty acids form the most stable esters.

At times it is preferable to allow only partial etherification or esterification thus forming half-ethers or half-esters instead of the di-ethers or di-esters theoretically possible. For other purposes the end-group hydroxyls may not only be partially or completely esterified or etherified, but also may be treated so as to result in the formation of mixed ethers, mixed esters or ether-esters.

Etherification or esterification of the end-groups may take place simultaneously with or subsequent to polymerization, and may be effected prior to or subsequent to the decolorizing and purifying processes described hereinbefore. Preferably, the end-group modification is carried out immediately after polymerization and before purification or decolorizing, but a secondary preferred time for modification is during the copolymerization step itself.

As stated hereinbefore, the polymeric lubricants prepared as described above have units of the general configuration



wherein R_1 is a hydrocarbon radical having at least two carbon atoms. R_1 may be either saturated or unsaturated. In the latter case, the polymers containing unsaturated linkages may be used as such as lubricants or may be hydrogenated, sulfurized, phosphorized or chlorinated with ease, in order to obtain products having modified properties, such as stability, extreme pressure, etc. These polymeric lubricants may contain modifying agents such as viscosity index improvers, stabilizers, anti-corrosion agents, gelling agents for the production of greases, as well as other materials.

The following examples illustrate preparation and properties of these synthetic lubricants:

Example I.—Copolymerization of alpha-butylene oxide and propylene oxide

One hundred parts alpha-butylene oxide, 100 parts propylene oxide and 400 parts isopentane were placed in a kettle fitted with a reflux condenser. Over a period of 2 hours 10 parts of boron trifluoride-ether complex was added. After 2½ hours the reaction mixture was washed with water, the volatile constituents removed under sub-atmospheric pressure and the polymeric product was dehydrated by heating at 100 C. under sub-atmospheric pressure. The resulting polymer was 180 parts of a yellow oil which had the following properties:

Centistokes viscosity at 100° F	53.16
Centistokes viscosity at 210° F	7.51
SAE	20
Viscosity index	112
Pour point, °F	—26

Example II.—Polymerization of alpha-butylene oxide

The procedure described in Example I was repeated, except that propylene oxide was omitted from the reaction mixture. The polymeric product had the following properties:

Centistokes viscosity at 100° F	51.76
Centistokes viscosity at 210° F	6.84
Viscosity index	94
SAE	20
Molecular weight	600
Freezing point, °C lower than	—75

Example III

The procedure described in Example I was repeated, except that propylene oxide was omitted from the polymerization mixture, while 1% by weight of methyl alcohol was added. The polymer obtained had the following properties:

Centistokes viscosity at 100° F	39.81
Centistokes viscosity at 210° F	5.56
Viscosity index	78
SAE	10
Molecular weight	444
Freezing point, °C lower than	—75

Example IV.—Polymerization of 1,2-epoxy-3-butene

The procedure described in Example I was repeated, using 1,2-epoxy-3-butene as the monomer instead of the mixture of monomers employed in Example I. The product had the following properties useful in a synthetic lubricant:

Centistokes viscosity at 100° F	79.2
Centistokes viscosity at 210° F	9.96
Viscosity index	113
SAE	20
Pour point, °F	—25
Freezing point, °C lower than	—75
Molecular weight	595

Example V.—Hydrogenation of polymerized 1,2-epoxy-3-butene

The polymer prepared as described in Example 4 was subjected to hydrogenation, using Raney nickel as the catalyst, at 110° C. and 1500 pounds hydrogen pressure for 24 hours. The polymer was dissolved in isopentane during the hydrogenation. The product so obtained had the following properties:

Centistokes viscosity at 100° F	65.9
Centistokes viscosity at 210° F	8.75
Viscosity index	113
SAE	20
Pour point, °F	—60
Freezing point, °C lower than	—75

We claim as our invention:

1. An oleaginous oleophilic mixture of homopolymeric ethers of 1,2-epoxybutane, suitable for use as a lubricating composition, said mixture having an average molecular weight between 444 and 600.

2. An oleaginous oleophilic mixture of homopolymeric ethers of 1,2-epoxy-3-butene, suitable for use as a lubricating composition, said mixture having an average molecular weight between 444 and 600.

3. An oleaginous oleophilic mixture of homopolymeric ethers of 1,2-epoxy linear hydrocarbons, suitable for use as a lubricating composition.

said epoxy hydrocarbons containing from 4 to 14 carbon atoms and bearing only hydrogen atoms and an epoxide ring on the 1,2-positions.

4. An oleaginous oleophilic mixture of homopolymeric ethers of 1,2-epoxybutane suitable for use as a lubricating composition.

5. An oleaginous oleophilic mixture of homopolymeric ethers of 1,2-epoxy-3-butene suitable for use as a lubricating composition.

6. An oleaginous oleophilic mixture of homopolymeric ethers of 1,2-epoxypentane suitable for use as a lubricating composition.

7. An oleaginous oleophilic mixture of homopolymeric ethers of 1,2-epoxy-3-pentene suitable for use as a lubricating composition.

8. An oleaginous oleophilic mixture of homopolymeric ethers of 1,2-epoxyoctane suitable for use as a lubricating composition.

9. An oleaginous oleophilic mixture of homopolymeric ethers of 1,2-epoxy linear hydrocarbons suitable for use as a lubricating composition, said epoxy hydrocarbons containing from four to fourteen carbon atoms and bearing only hydrogen atoms and an epoxide ring on the 1,2 positions, said mixture having a freezing point below −75° C.

SEAVER A. BALLARD.
RUPERT C. MORRIS.
JOHN L. VAN WINKLE.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,149,498	Bludworth	Mar. 7, 1939
2,187,006	Alvarado	Jan. 16, 1940
2,233,382	De Groote	Feb. 5, 1941
2,293,868	Toussaint	Aug. 25, 1942
2,309,722	Wilkes	Feb. 2, 1943
2,344,886	Lieber	Mar. 21, 1944
2,364,248	Freuler	Dec. 5, 1944
2,369,632	Cook	Feb. 13, 1945
2,383,915	Morgan	Aug. 28, 1945
2,425,755	Roberts	Aug. 19, 1947
2,425,845	Toussaint	Aug. 19, 1947