

Description

This invention relates to polyesters, and in particular to succinic group based polyesters. These polyesters find utility in lubricants as friction reducers and as viscosity improvers, and enhance film-forming properties of base oils.

In the operation of modern internal combustion engines, it is desirable, and often necessary because of government regulation, to obtain maximum fuel economy. From a purely economic standpoint, with the increasing cost and, from time to time, shortages of hydrocarbon fuels, improving the fuel efficiency of internal combustion engines is very desirable. Accordingly, methods for improving fuel economy have been the subject of numerous patents, including U.S. 4,584,115, U.S. 4,237,022, and U.S. 4,406,802.

Many polymeric materials have been developed for use as viscosity improvers. The purpose of viscosity improvers is to minimize the changes in viscosity of an oil composition when it is exposed to a variety of temperatures. Included among viscosity improvers known in the art are polyolefins, styrene-butadiene copolymers, high molecular weight polyesters, and the like. Examples of such products appear in U.S. 2,394,909, U.S. 3,598,738, U.S. 3,772,169, and U.S. 3,795,616.

Recently, efforts have been directed toward preparing additives for lubricants and fuels which have multifunctional properties. The advantages of such multifunctional additives are obvious. For example, it is often less costly to prepare a single additive having multifunctional characteristics, rather than preparing several additives, each having a single characteristic. When such multifunctional additives are available, it is not necessary to have a multitude of storage tanks to store a variety of additives for blending. Storage space requirements and shipping costs are often reduced when the multifunctional additive provides, on a reduced weight basis, the same performance as two or more additives which each provide a single function. Examples of well-known multifunctional additives are dispersant-viscosity improvers, basic metal salts which have antioxidant properties, and the like.

Certain polysuccinate esters are known. U.S. Patent 2,993,773 describes numerous esters of alkenyl, succinic acids and anhydrides, and the use thereof as deposit modifiers in fuels. Mixed esters of polyhydric alcohols and the use thereof as synthetic oils are described in U.S. Patent 2,575,196. U.S. Patent 2,134,736 refers to mono and polyhydric alcohol esters of polybasic carboxylic acids as additives for lubricating oils. There is no suggestion of polyesters. U.S. Patent 2,394,909 refers to polyesters having average molecular weights between 5000 and 25,000 as viscosity improvers for lubricants. U.S. Patent 2,561,232 describes diesters derived from dibasic acids and monohydric alcohols. U.S. Patent 2,570,037 relates to diesters derived from dibasic acids and ether-alcohols. U.S. Patent 2,929,786 describes synthetic lubricating oil compositions wherein a reaction product of a dibasic acid and a glycol is employed as the synthetic lubricant or as an additive for a synthetic lubricant. U.S. Patent 3,381,022 describes polyesters which have a high molecular weight substituent on the succinic group. U.S. Patent 4,209,411 describes polyesters derived from a hydrocarbon substituted succinic anhydride and a cyclic poly(methylol) compound.

We have found it possible to provide additives for lubricants which provide improved frictional characteristics and which, when used in lubricating oils, provide fuel economy improving benefits. We have further found it possible to provide lubricants which impart improved fuel economy benefits. We have also found it possible to provide additives which improve the viscosity characteristics of lubricating oils. We have still further found it possible to provide lubricants having improved viscosity properties. We have additionally found it possible to provide additives for lubricants, which additives have multifunctional characteristics.

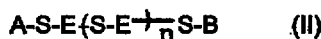
Thus, in one aspect the invention provides lubricating compositions comprising a major amount of a mineral oil of lubricating viscosity and a minor amount of at least one polysuccinate ester having a molecular weight between 1000 and 4000, and which is substantially free of cycloaliphatic groups, and wherein the succinic groups contain alkyl or alkenyl substituents each having from 4 to 28 carbon atoms. The polysuccinate esters provide viscosity improving and friction reducing properties to the lubricating oil. The above-described polyesters are preferably prepared by the condensation reaction of

(A) at least one alkyl or alkenyl substituted succinic acid or anhydride, wherein the alkyl or alkenyl substituent contains from 4 to 28 carbon atoms with

(B) at least one open-chain aliphatic compound having at least two OH groups, wherein the ratio of reactant A to B is from 1 succinic group:1.8 OH groups to 1 succinic group:4 OH groups.

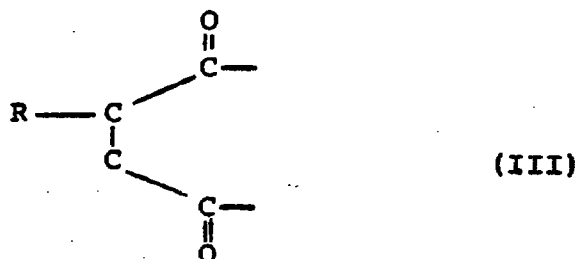
An alternative means for preparing polyesters useful in the lubricating compositions of this invention comprises the condensation reaction of component (A) with (C), at least one epoxide.

This invention also relates to a polysuccinate ester of the formula

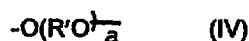


wherein n is a number between 1 and 8,

each S is a group of the formula



wherein R is an alkyl or alkenyl group having from 4 to 28 carbon atoms, and each E is a group of the formula



wherein R' is selected from

alkylene groups having from 2 to 28 carbon atoms, hydroxy substituted alkylene groups having from 2 to 28 carbons, and containing from one to 6 hydroxy groups, with the proviso that the number of hydroxy groups does not exceed the unsatisfied valences of R', and

succinate ester substituted alkylene groups, and wherein a is a number of from 1 to 8, wherein each A and each B is independently

-OH, -OR², wherein R² is an alkyl group containing from 1 to 28 carbons, -O(R'O)_bH, wherein R' is an alkylene group containing from 2 to 28 carbon atoms, and b is a number ranging from 1 to 8, and

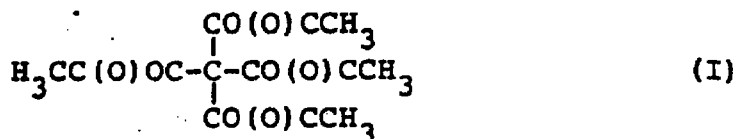
-NR³, wherein each R³ is independently H or an alkyl group having from 1 to 18 carbon atoms, with the proviso that at least one of A or B is not -OH, or, when A or B is -OH, that is, when the terminal group contains a carboxylic acid group, a salt may be formed by reaction with a basic metal containing reagent, ammonia or an amine,

and which polysuccinate ester has a molecular weight between 1000 and 4000, and lubricating oil compositions comprising a major amount of a mineral oil of lubricating viscosity and a minor amount of the polysuccinate ester of formula (II).

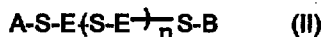
Methods for improving fuel economy employing the lubricating compositions of this invention are described. Preferred features and embodiments of the invention are hereinafter described.

The lubricating oil compositions comprise polysuccinate esters having a molecular weight between 1000 and 4000, and wherein the succinic groups within the polymer have alkyl or alkenyl substituents each having from 4 to 28 carbon atoms.

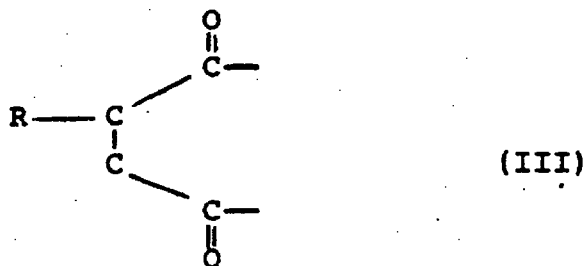
The expression "polyester" is broadly defined in the art as a material containing a plurality of ester groups. Thus, a compound of the formula



could be considered a polyester. In the context of this invention, the expression polyester is intended to encompass only those materials which are polymeric polyesters. That is, the polysuccinate esters of this invention are polymers containing multiple ester linkages, and have the general formula



wherein n is a number between 1 and 8, each S is a group of the formula



wherein R is an alkyl or alkenyl group having from 4 to 28 carbon atoms, and each E is a group of the formula



wherein R' is selected from the group consisting of

alkylene groups having from 2 to 28 carbon atoms, preferably those having 2 or 3 carbon atoms, hydroxy substituted alkylene groups having from 2 to 28 carbons, and containing from one to 6 hydroxy groups, with the proviso that the number of hydroxy groups does not exceed the unsatisfied valences of R', and

succinate ester substituted alkylene groups, and wherein a is a number ranging from 1 to 8, preferably 1 or 2, and each A and each B is independently

-OH,

-OR², wherein R² is an alkyl group containing from 1 to 28 carbons,

-O(R'O)_bH, wherein R' is an alkylene group containing from 2 to 28 carbon atoms, more often 2 or 3 carbons, and b is a number ranging from 1 to 8, preferably 1 or 2, and

-NR₃, wherein each R³ is independently H or an alkyl group having from 1 to 18 carbon atoms, with the proviso that at least one of A or B is not -OH, or, when A or B is -OH, that is, when the terminal group contains a carboxylic acid group, a salt may be formed by reaction with a basic metal containing reagent, ammonia or an amine, preferred metals being sodium, potassium, calcium, zinc and copper, and which polysuccinate ester has a molecular weight between 1000 and 4000.

Thus, the polysuccinate ester may contain other polyester branches, including other polysuccinate ester branches, but the main polyester chain must have the polymeric polyester structure described hereinabove.

The polysuccinate esters may be prepared in a variety of ways. One method is to react an epoxide with an alkyl or alkenyl substituted succinic anhydride at a temperature between 125 to 225° C, preferably between 140 to 170°C, usually in the presence of a tertiary amine catalyst. A general procedure is set forth in U.S. 3,381,022.

Other procedures for preparing polysuccinate esters are likewise described in this patent.

The polysuccinate esters of this invention preferably contain a minimal number of unreacted carboxylic groups. The amount of unreacted carboxylic acid remaining can be determined by measuring the acid number of the polysuccinate ester employing the method described in American Society for Testing and Materials D-974.

Although it is generally preferred to minimize the unreacted carboxylic acid remaining in the polyesters, it is not always critical, and it is sometimes advantageous, if the polyester contains some unreacted carboxylic acid. Accordingly, depending on the extent of reaction, whether the unreacted carboxylic acid groups have been further reacted to "cap" the polyester, and also, on the molecular weight of the polymer, the acid number may be between 0, that is, free of carboxylic acid, to 60.

The acid number of the polysuccinate ester depends on several factors including the size of the substituents on the succinic groups, the extent of polymerization and the number of carboxylic acid groups present on the polysuccinate ester. Preferably, the polysuccinate ester has at least 50% of the possible terminal carboxylic acid groups converted to ester groups, amido groups, salts or mixtures thereof. Polysuccinate esters having acid numbers up to 30, preferably between 10 and 20 are often useful additives for the lubricating oil compositions of this invention.

As mentioned hereinabove, the polysuccinate esters employed in the lubricating oils of this invention have a molecular weight between 1000 and 4000. Preferably, the polysuccinate esters have molecular weights between 1500 and 4000, often between 1500 and 3000, and frequently between 2000 and 3000.

It has been found that polyesters having molecular weights between 1000 and 4000 have exceptional stability towards mechanical shear, which permits these, polymers to be employed in lubricating oils subjected to high shear conditions, such as in lubricants for gear oils and modern internal combustion engines.

Methods for determining molecular weights of polymers are well known in the art. Such methods include gel permeation chromatography, boiling point elevation, vapor phase osmometry and others. Textbooks on general polymer chemistry, including "Macromolecules, An Introduction to Polymer Science", F. A. Bovey and F. H. Winslow, Editors, Academic Press, New York (1979), pages 296-316, and P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press (1953) Chapter VII, pages 266-316, describe these methods. It has been found that vapor phase osmometry (VPO) is a particularly useful method for determining number average molecular weights of the polysuccinate esters of this invention.

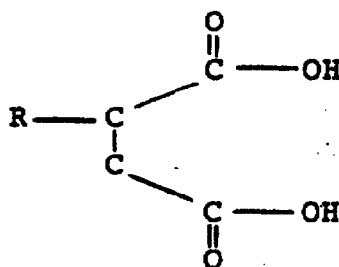
Gel permeation chromatography is an effective tool for measuring molecular weights, particularly when the instrument is calibrated against known compounds of similar structure and molecular weight.

The substituent on the succinic group of the polysuccinate esters may contain from 4 to 28 carbon atoms. When it is desired that the polymer of this invention provides fuel economy improving benefits, it is usually desirable that the alkyl or alkenyl group contain at least 8, and preferably at least 12 carbon atoms. Particularly desirable polyesters for use as fuel economy improving and friction reducing additives will have at least one substituent containing from 12 to 24 carbons, more often from 14 to 18 carbons. The substituent on the succinic group may be linear or branched chain. When it is desired to use the polymer as a friction reduced, it has been found that a substituent comprising a straight chain segment containing at least 8 carbon atoms, more preferably 12 carbon atoms is desirable. These substituents correspond to the group R in formula (II).

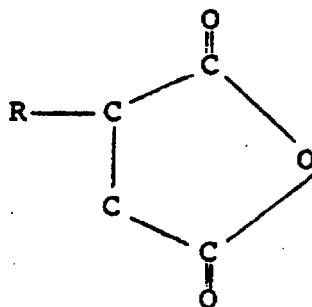
The polysuccinate esters are preferably glycol esters, glycerol esters, pentaerythritol esters or neo-diol esters. Neo-diol esters are particularly stable.

The polysuccinate esters are preferably derived from alkyl or alkenyl substituted succinic acids or anhydrides which have been reacted with certain polyhydric alcohols and which may then be further reacted with an additional reagent reactive with carboxylic acids to "cap" the polymer by reacting with any remaining carboxylic acid groups.

The polysuccinate esters (A) of this invention are preferably derived from substituted succinic acids of the formula



or substituted succinic anhydrides of the formula



wherein R is an alkyl or alkenyl group containing from 4 to 28 carbon atoms. The alkyl or alkenyl groups themselves may contain other substituents which do not significantly alter the essentially alkyl or alkenyl character of the group. Such substituents include, but are not necessarily limited to, halogen, such as chlorine, alkoxy, such as methoxy, and the like. Preferably there will be no more than one such substituent for every 10 carbon atoms of alkyl or alkenyl substituent. Most preferred is when the alkyl or alkenyl substituents are purely hydrocarbyl, that is, no more than an impurity amount of atoms other than carbon or hydrogen are present in the alkyl or alkenyl group.

The substituted succinic acids or anhydrides employed in the process of this invention are prepared by

methods well known to those skilled in the chemical arts. Several methods are given in U.S. 2,993,773 and U.S. 2,394,909.

A preferred method involves reaction of maleic anhydride with a monoolefinic monomer or oligomer at 100-200°C with or without a catalyst to form the corresponding substituted succinic anhydride. The succinic anhydride can be hydrolyzed by heating with water to form the corresponding succinic acid.

Although the source of the alkyl or alkenyl based substituent is not a critical aspect of this invention, this substituent will generally be derived from various olefinic monomers such as ethylene, propylene, butylene, hexene, octene, decene, etc, including the oligomers, prepolymers and low molecular weight polymers formed from the foregoing monomers. Thus, dimers, trimers and/or tetramers of propylene and butylene can be used.

As mentioned hereinabove, the polysuccinate esters used in the lubricating oils of this invention can be prepared by various reactions with succinic acids or anhydrides. One of the mentioned reactions involves the condensation of a succinic anhydride as described hereinabove with an epoxide. Particularly useful epoxides for this reaction are those derived from alpha-olefins. Improved frictional properties are obtainable when the alpha-olefin epoxide contains a straight-chain segment of at least 8 carbons, preferably at least 12 carbons, and up to 28 carbons. Epoxides having straight-chain segments containing from 12 to 24 carbon atoms, more often from 14 to 18 carbons, are especially preferred. Particularly preferred is when the straight-chain segment is an alkyl or alkenyl group.

In the method which is preferred because of convenience and superior properties of the esters obtained, the polyester is prepared by the condensation reaction of a suitable polyhydric alcohol with the substituted succinic acids or anhydrides described hereinabove.

The reaction between the succinic acid or anhydride and the polyhydric alcohol is normally conducted at a temperature from 150°C up to the lowest temperature at which one of the reactants undergoes significant decomposition. Preferably, the reaction is conducted at no more than about 250°C, more preferably between 175 to 225°C.

Depending on the size of the batch, the reaction may be conducted for a period of from 5-8 hours for a small laboratory batch of a few liters up to 24 hours or more for larger scale pilot plant or manufacturing batch. Also, the duration of reaction may be dictated by the desired molecular weight and acid number of the product. That is, to prepare a higher molecular weight polyester, or one having a relatively low acid number may require a longer reaction time than will a product with a low molecular weight or higher acid number. Prolonged heating beyond the time necessary to attain a product having the desired characteristics, besides being wasteful, also may result in further condensation of polymers in the reaction mixture which could result in formation of substantial amounts of polymers having molecular weights higher than desired.

It is often helpful to monitor the reaction to determine the molecular weight of the reaction product during the course of the reaction. This is generally accomplished by periodically withdrawing samples from the reaction mixture and measuring the molecular weight of the polyester contained therein. A particularly useful means for determining the molecular weight of the polyester in the reaction mixture is to employ gel permeation chromatography (GPC) or high-speed GPC. The instrument preferably is calibrated employing polyesters of the type and molecular weight range of the polyesters being analyzed. Other methods, such as vapor phase osmometry, while useful for determining the molecular weight of the polyester product, may be influenced by impurities, unreacted components, etc., present in a crude reaction mixture before workup.

The polyhydric alcohols useful in the preparation of the polysuccinate esters may contain up to 8 hydroxyl groups, and may be linear or branched. For example, glycerol, containing 3 hydroxy groups is linear and pentaerythritol, with four hydroxyl groups, is branched. Neopentylene glycol, with 2 hydroxyl groups, is branched. Thus, the expressions "branched" or "linear" refer to the configuration of the hydrocarbon backbone of the polyhydric alcohol. Preferred polyhydric alcohols are ethylene glycol, neopentylene glycol, glycerol and pentaerythritol. Mixtures of polyhydric alcohols may be used. Diols usually result in essentially linear polysuccinate esters, whereas triols and higher polyhydric alcohols may result in the formation of branched polysuccinate esters. Also, tri- and higher polyhydric alcohols can provide polyesters containing hydroxyl groups. Ethylene glycol is an especially preferred polyhydric alcohol for preparing the polysuccinate esters used in the lubricating oils of this invention.

The polyhydric alcohols used in the preparation of the polysuccinate esters of this invention also may include polyethers or partial fatty acid esters of polyols. Useful polyethers include polyhydroxy polyalkoxy alkanes, such as diethylene glycol. Useful partial fatty acid esters will contain at least two hydroxyl groups. Glycerol monooleate is illustrative.

The polyhydric alcohol will generally contain from two to 28 carbons. As mentioned hereinabove, one way of providing fuel economy benefits is to have substituents in the succinic group containing at least 8 carbon atoms, preferably, a straight-chain segment containing at least 8 carbon atoms. Improved frictional properties can also be obtained when the polyhydric alcohol contains a linear, terminal hydrocarbon segment containing

at least 8 carbon atoms, preferably at least 12 carbon atoms. Polyesters providing friction modifying and fuel economy benefits often will contain from 12 to 24 carbon atoms, frequently from 14 to 18 carbon atoms in the terminal hydrocarbon segment described above. For example, a 1,2-alkane diol, such as 1,2-hexadecanediol, can be reacted with a succinic anhydride having hydrocarbon substituents containing 4 carbon atoms. The resulting polyester can be used as a fuel economy improving agent.

The polysuccinate esters of this invention may have acid numbers ranging between 0 and 60. Thus, a certain number of carboxylic acid groups may remain unreacted. The extent of reaction of the substituted succinic acid or anhydride with the polyhydric alcohol and the formula weights of the reactants will influence the acid number of the resulting polyester. As discussed hereinbelow, the polyester may be further reacted with other reagents to further reduce the acid number.

It has been found that the stoichiometric ratio of reactants and the nature of the polyhydric alcohol are the most important factors in determining the molecular weight of the polyesters prepared therefrom. In order to minimize the number of unreacted carboxylic acid groups present in the polysuccinate esters used in the lubricating oil compositions of this invention, the stoichiometric ratio of succinic acid (or anhydride) to equivalents of hydroxyl groups available on the polyhydric alcohol must be considered. It has been found that at least 1.8 OH groups should be reacted with each succinic group, which contains two potentially reactive carboxylic groups. Depending on other considerations, such as steric hindrance of the polyhydric alcohol, a greater ratio of available OH groups may be present in the reaction mixture for each succinic group. When the polyhydric alcohol is a diol, it is preferred to employ the reactants in a ratio in the range of from 1.8 to 2.3 OH groups for each succinic group. For higher polyhydric alcohols, particularly sterically hindered polyhydric alcohols, a ratio in the range of from 2.9 to 4 OH groups per succinic group is often preferred. It is sometimes desirable, for example, when employing a volatile polyhydric alcohol, to employ an excess of polyhydric alcohol to compensate for loss of volatile reactant. Usually a ratio between 1.8 and 4 OH groups per succinic group will provide a satisfactory polysuccinate ester.

If it is desired to reduce the number of carboxylic acid groups present in the polysuccinate ester, the ester may be further reacted with other reagents reactive with carboxylic acids. Thus, the polysuccinate ester may be reacted with other reagents such as amines, basic metal compounds, alcohols and the like. This reaction is often referred to as "capping". Capping may take place by reaction of a polysuccinate ester which contains carboxylic acid groups, with a monohydric alcohol, a diol, a lower amine having at least one N-H group, an isocyanate, or a metal-containing reagent. When the "capping reagent" contains more than one site reactive with a carboxylic acid, care must be taken, such as minimizing reaction time, to avoid increasing the molecular weight of the polysuccinate ester which could take place if two carboxylic acid group containing polysuccinate ester compounds are further reacted with a single polyfunctional "capping reagent". Accordingly, it is preferred that the "capping reagent" is a monofunctional reagent such as a lower monohydric alcohol, an ethoxylated alcohol, a monoamine and the like. Illustrative examples include methanol, dibutylamine, N,N-diethyl ethanamine and the like. When the capping reagent is an alcohol, catalysts such as those described elsewhere in this specification for use in similar reactions, may be used, and are usually preferred.

Although the polysuccinate esters useful in this invention can be prepared in the absence of catalysts, catalysts are often employed. Tertiary amines, especially lower alkyl tertiary amines (i.e., each alkyl has no more than seven carbons) are very useful catalysts for the condensation reaction of substituted succinic anhydrides with epoxides. Various metal-containing compounds serve as catalysts for esterification of a carboxylic acid moiety with an OH-containing reagent. Particularly useful catalysts are titanium alkoxides, aluminum alkoxides, and certain metal-containing bases including Sb_2O_3 , SnO_2 and PbO_3 . Catalysts such as sulfuric acid, pyridine hydrochloride, hydrochloric acid, benzene sulfonic acid, p-toluene sulfonic acid, phosphoric acid, or any other known esterification catalyst may be used. Other materials useful as catalysts will occur to the skilled worker. The amount of the catalyst in the esterification reaction may be as little as 0.01% by weight of the reaction mixture, more often from 0.1% to 5%.

If a polyester is found to have too low a molecular weight, one of the metal-containing catalysts, such as titanium isopropoxide, can be injected into the reaction mixture, together, if deemed appropriate, with additional polyhydric alcohol or anhydride (or diacid) to rebalance the carboxylic acid:OH ratio and induce coupling of the polyester to higher molecular weight products.

It is frequently useful if the polyester contains hydroxyl groups. The hydroxyl group moiety is a polar group which provides surface activity to the polyester. That is, the polyester is attracted at the polar hydroxyl groups to the metal being lubricated. Means for incorporating hydroxyl groups into the polyester include controlling reaction conditions such that a portion of the hydroxyl groups of the polyhydric alcohol reactant remains unreacted. Such means include charging a stoichiometric excess of polyhydric alcohol reactant relative to succinic reactant, controlling the extent of reaction, e.g., by limiting reaction duration, operating at lower temperatures, and the like.

The following examples illustrate several intermediates and polysuccinate esters prepared therefrom. These examples are presented for illustrative purposes only, and are not intended to be considered as limiting the scope of this invention. Unless indicated otherwise, temperatures are in degrees Celsius.

6 Example 1

To a reaction vessel containing 1896 parts of maleic anhydride is added 4446 parts of a commercial mixture of C₁₅₋₁₈ predominantly straight-chain alpha-olefins. The mixture is heated to reflux under nitrogen, and the temperature is allowed to increase to 210°C over 16 hours. The material is stripped to 210°C at 1.3 kPa (10 Torr) to remove volatiles and the residue is filtered with a diatomaceous earth filter aid. The filtrate is the desired substituted succinic anhydride.

Example 2

15 Following substantially the procedure of Example 1, a commercial mixture of C₁₈₋₂₄ olefins, comprising predominantly vinyl and vinylidene group-containing alpha-olefins, is reacted with maleic anhydride.

Example 3

20 To a one-liter, four-necked flask equipped with a stirrer, thermowell, a sub-surface nitrogen sparge tube and a Dean-Stark water trap with a reflux condenser, is charged 303 parts of a reaction product prepared according to the procedure of Example 1, and 68 parts of ethylene glycol. The mixture is heated to 151°C over two hours with a sub-surface nitrogen sparge, until water evolution begins. Water is collected in the Dean-Stark trap. Heating is continued for a total of 24 hours while the temperature increases to 176°C and water is collected. 25 Water evolution is essentially complete after about 9-10 hours, but the acid number as determined by ASTM-D974 continues to decrease until the residue has an acid number of about 17. The reaction mixture is stripped to 170°C at 930 Pa (7 Torr), and the viscous residue is filtered through a diatomaceous earth filter aid at 150°C.

Example 4

30 Following essentially the same procedure as Example 3, 414 parts of a substituted succinic anhydride prepared essentially according to the procedure of Example 2 is reacted with 68 parts of ethylene glycol. The product has an acid number as measured by ASTM-D974 of about 15.

35 Example 5

A two-liter, four-necked flask equipped with a stirrer, thermowell, a Dean-Stark water trap with reflux condenser is charged with 447 parts of a succinic anhydride prepared essentially according to the procedure of Example 2. 95 parts 2-butyne-1,4,diol are added, and the materials are heated to melting. The reaction is run 40 at 120°C (reflux) for two hours, while collecting 5 milliliters water in the Dean-Stark tube. While stirring, 4 parts tetraisopropyltitanate is added followed by heating at 200°C for 7 hours. The materials are stripped to 120°C at 2.4 kPa (18 Torr), then filtered through a diatomaceous earth filter aid.

Example 6

45 A 2-liter, 4-necked reactor equipped with a nitrogen sparge tube, mechanical stirrer, thermowell and reflux condenser is charged with 360 parts of a commercial C₁₈ alpha-olefin epoxide, 672 parts of a succinic anhydride prepared essentially according to the procedure of Example 2, and 7.5 parts tributyl amine. The mixture is heated to 125°C and held for 1 hour. The temperature is raised to 150°C and held at 150-155°C for 4 hours. 50 The temperature is increased to 179°C for 5 hours after an additional 7.5 parts tributyl amine is added. 18 parts additional epoxide is added and the reaction mixture is stirred at 150-155°C for one hour. The infrared spectrum indicates residual anhydride. Additional 18 parts epoxide is added and the reaction is continued at 150-155°C for 1.5 hours. A nitrogen sparge is continued throughout the reaction. The reaction mixture is then filtered through a diatomaceous earth filter aid. The product has a number average molecular weight as measured by vapor 55 phase osmometry of 1075.

Example 7

330 parts of a polyester prepared according to the procedure of Example 3 is reacted with 4 parts of CH_3OH in the presence of tetraisopropyl titanate catalyst at 155°C for 3 hours.

Example 8

330 parts of a polyester prepared according to the procedure of Example 3 is reacted with 7 parts of di(n-butyl)amine and vacuum stripped to remove unreacted amine.

Example 9

425 parts of a polyester prepared according to the procedure of Example 4 is reacted at room temperature with 18 parts of t- C_{12-14} primary amine (Primene 81R - Rohm and Haas).

Example 10

425 parts of a polyester prepared according to the procedure of Example 4 is reacted with 6 parts of ethylene glycol at 150°C for 0.5 hours.

Example 11

A 3-liter, 4-necked flask equipped with a stirrer, thermowell, a nitrogen sparge and a Dean-Stark water trap with a reflux condenser is charged with 303 parts of the substituted succinic anhydride of Example 1 and 90 parts of ethylene glycol. The reaction mixture is heated to 150°C and held at $150-158^\circ\text{C}$ over 18 hours. Water (7.9 ml) is removed. 142 parts of stearic acid is charged to the flask over 0.1 hours and is heated to 160°C over 16 hours while collecting an additional 4.8 ml H_2O . The product is stripped to 180°C at 1.3 kPa (10 Torr) followed by filtration through cloth and diatomaceous earth at 150°C . The product has a number average molecular weight as determined by gel permeation chromatography of 1790.

Example 12

A 1-liter flask equipped in the same fashion as that of Example 11 is charged with 227 parts of the succinic anhydride of Example 1, 106 parts of that of Example 2 and 96 parts of ethylene glycol. The reaction is conducted at $150-168^\circ\text{C}$ over 14 hours while collecting 6.8 ml H_2O . 142 parts stearic acid is charged and the temperature is increased to 180°C over 2 hours and held at $180-188^\circ\text{C}$ over 5 hours while collecting 6.8 ml H_2O . The mixture is stripped to 180°C at 2 kPa (15 Torr) and the residue is filtered as in Example 11. The product has a number average molecular weight by gel permeation chromatography of 1610.

Example 13

Following essentially the procedure of Example 6, 240 parts of C_{16} alpha-olefin epoxide and 265 parts of n-dodecenyl succinic anhydride are reacted in the presence of 5 parts of tributylamine. The product obtained has a number average molecular weight of 1754, determined by vapor phase osmometry.

Example 14

A 500 milliliter flask is equipped with a stirrer, Dry Ice-isopropanol condenser and gas inlet tube, is charged with 250 parts of the product of Example 13 and is heated to 110°C . Ethylene oxide is passed into the reactor contents at 0.2 moles/hour over 2.5 hours, at $110-115^\circ\text{C}$. The polyester product has an acid number (ASTM D-974) of 3.8.

Example 15

A 1-liter flask equipped with a stirrer, thermowell, N_2 sparge and Dean-Stark trap with condenser is charged with 303 parts of the succinic anhydride of Example 1 and 148 parts of a C_{14-15} linear primary alcohol (Neodol[®] 45, Shell Chemical). The mixture is heated to 100°C and held at 100°C for 2 hours followed by charging 42

parts ethylene glycol. The reaction mixture is heated to 180°C over 8 hours; H₂O evolution begins at about 170°C. The reaction is continued at 180°C for 4 hours. 7.6 ml of H₂O is collected. The mixture is stripped to 180°C at 2 kPa (15 Torr). The residue is filtered at 150°C through cloth and a diatomaceous earth filter aid. The product has a number average molecular weight of 1130 as determined by gel permeation chromatography.

Example 16

A 2-liter flask is charged with 921 parts glycerine and purged with N₂ at 2 cubic feet per hour flow rate while stirring. 10 parts NaOH powder is added and the mixture is heated to 255°C. The reaction is continued at 255-260°C for 1.5 hours while collecting water of evolution in a Dean-Stark water trap. A total of 132 parts H₂O is collected. The product has a %OH=37.58 by analysis.

Example 17

A 1-liter flask equipped with a stirrer, thermometer, Dean-Stark trap with condenser and N₂ sparge is charged with 236.5 parts of the product of Example 2 and 100 parts of the product of Example 16. The reaction is conducted at about 200°C while removing H₂O. When H₂O evolution essentially ceases, 202 parts of a 100 neutral oil is added, the materials are mixed thoroughly and filtered with a diatomaceous earth filter aid. The product has an acid number of about 2.5-3.0.

The Mineral Oil of Lubricating Viscosity

The lubricating compositions and methods of this invention employ a mineral oil of lubricating viscosity. Mineral lubricating oils include those such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful.

Unrefined, refined and rerefined mineral oils, of the type disclosed hereinabove can be used in the compositions of the present invention. Unrefined oils are those obtained directly without further purification treatment. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Rerefined oils are obtained by processes similar to those used to obtain refined oils, applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

Specific examples of many of the above-described oils of lubricating viscosity are given in Chamberlin III, U.S. 4,326,972, and European Patent Application 107,282.

A basic, brief description of lubricant base oils appears in an article by D. V. Brock, "Lubrication Engineering", Volume 43, pages 184-5, March, 1987.

The polysuccinate esters are used in the mineral oil lubricating compositions of this invention at levels adequate to provide viscosity improving and/or fuel economy improving benefits. They are generally used in minor amounts in lubricating oil blends. They may be present at levels ranging from 0.1 to 35 percent by weight of the lubricating oil compositions, more often from 1 to 20 percent by weight. Preferably, they are present at 2 to 10 percent by weight.

Other Additives

The compositions of this invention may contain other components. The use of such additives is optional and the presence thereof in the compositions of this invention will depend on the particular use and level of performance required. The compositions may comprise a zinc salt of a dithiophosphoric acid. Zinc salts of dithiophosphoric acids are often referred to as zinc dithiophosphates, zinc 0,0-dihydrocarbyl dithiophosphates, and other commonly used names. They are sometimes referred to by the abbreviation ZDP. One or more zinc salts of dithiophosphoric acids may be present in a minor amount to provide additional extreme pressure, anti-wear and anti-oxidancy performance.

In addition to zinc salts of dithiophosphoric acids discussed hereinabove, other additives that may be used in the lubricating oils of this invention include, for example, detergents, dispersants, oxidation inhibiting agents, pour point depressing agents, extreme pressure agents, anti-wear agents, color stabilizers and anti-foam agents.

Extreme pressure agents and corrosion and oxidation inhibiting agents which may be included in the compositions of the invention are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax and

organic sulfides and polysulfides. Also contemplated are phosphorus esters.

Other viscosity improvers may be included in the lubricating oil compositions of this invention. Examples include polymethacrylic acid esters, diene polymers, polyalkyl styrenes, alkenylarene-conjugated diene copolymers and polyolefins. Multifunctional viscosity improvers which also have dispersant and/or antioxydancy properties are known. Such products are described in numerous publications including Dieter Klamann, "Lubricants and Related Products", Verlag Chemie GmbH (1984), pp 185-193; C. V. Smalheer and R. K. Smith, "Lubricant Additives", Lezius-Hiles Co (1967); M. W. Ranney, "Lubricant Additives", Noyes Data Corp. (1973), pp 92-145; M. W. Ranney, "Lubricant Additives, Recent Developments", Noyes Data Corp (1978), pp 139-164; and M. W. Ranney, "Synthetic Oils and Additives for Lubricants", Noyes Data Corp. (1980), pp 96-166.

Pour point depressants are a particularly useful type of additive often included in the lubricating oils described herein. The use of such pour point depressants and oil-based compositions to improve low temperature properties of oil-based compositions is well known in the art. See for example, page 8 of "Lubricant Additives" by C. V. Smalheer and R. Kennedy Smith (Lezius-Hiles Company Publishers, Cleveland, Ohio, 1967). Pour point depressants useful for the purpose of this invention, techniques for their preparation and their use are described in U.S. Patent numbers 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,748; 2,721,877; 2,721,878; and 3,250,715.

Anti-foam agents are used to reduce or prevent the formation of stable foam. Typical anti-foam agents include silicone or organic polymers. Additional anti-foam compositions are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162.

Detergents and dispersants may be of the ash-producing or ashless type. The ash-producing detergents are exemplified by oil soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, phenols or organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage.

The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. Basic salts and techniques for preparing and using them are well known to those skilled in the art and need not be discussed in detail here.

Ashless detergents and dispersants are so-called despite the fact that, depending on its constitution, the detergent or dispersant may upon combustion yield a non-volatile residue such as boric oxide or phosphorus pentoxide; however, it does not ordinarily contain metal and therefore does not yield a metal-containing ash on combustion. Many types are known in the art, and any of them are suitable for use in the lubricants of this invention. The following are illustrative:

(1) Reaction products of carboxylic acids (or derivatives thereof) containing at least about 34 and preferably at least about 54 carbon atoms with nitrogen containing compounds such as amine, organic hydroxy compounds such as phenols and alcohols, and/or basic inorganic materials. Examples of these "carboxylic dispersants" are described in British Patent number 1,306,529 and in many U.S. patents including the following

	3,163,603	3,351,552	3,541,678
	3,172,892	3,381,022	3,542,680
5	3,184,474	3,399,141	3,567,637
	3,215,707	3,415,750	3,574,101
	3,219,666	3,433,744	3,576,743
10	3,271,310	3,444,170	3,630,904
	3,272,746	3,448,048	3,632,510
	3,281,357	3,448,049	3,632,511
15	3,306,908	3,451,933	3,697,428
	3,311,558	3,454,607	3,725,441
	3,316,177	3,467,668	4,194,886
	3,340,281	3,501,405	4,234,435
20	3,341,542	3,522,179	4,491,527
	3,346,493	3,541,012	RE 26,433

(2) Reaction products of relatively high molecular weight aliphatic or alicyclic halides with amines, preferably polyalkylene polyamines. These may be characterized as "amine dispersants" and examples thereof are described for example, in the following U.S. patents:

	3,275,554	3,454,555
30	3,438,757	3,565,804

(3) Reaction products of alkyl phenols in which the alkyl groups contains at least about 30 carbon atoms with 25 aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines), which may be characterized as "Mannich dispersants". The materials described in the following U.S. patents are illustrative:

	3,413,347	3,725,480
40	3,697,574	3,726,882
	3,725,277	

(4) Products obtained by post-treating the carboxylic, amine or Mannich dispersants with such reagents as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus compounds or the like. Exemplary materials of this kind are described in the following U.S. patents:

	3,036,003	3,282,955	3,493,520	3,639,242
	3,087,936	3,312,619	3,502,677	3,649,229
5	3,200,107	3,366,569	3,513,093	3,649,659
	3,216,936	3,367,943	3,533,945	3,658,836
	3,254,025	3,373,111	3,539,633	3,697,574
10	3,256,185	3,403,102	3,573,010	3,702,757
	3,278,550	3,442,808	3,579,450	3,703,536
	3,280,234	3,455,831	3,591,598	3,704,308
	3,281,428	3,455,832	3,600,372	3,708,522
15				4,234,435

(5) Interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides and poly-(oxyethylene)-substituted acrylates. These may be characterized as "polymeric dispersants" and examples thereof are disclosed in the following U.S. patents:

	3,329,658	3,666,730
25	3,449,250	3,687,849
	3,519,565	3,702,300

The other members of above-illustrated optional additives may each be present in minor amounts in lubricating compositions at a concentration of as little as 0.001 percent by weight, usually ranging from 0.01 percent to 20 percent by weight. In most instances, they each may be present from 0.1% to 10% by weight.

The various additives described herein can be added directly to the lubricant. Preferably, however, they are diluted with a substantially inert, normally liquid organic diluent such as mineral oil, naphtha, benzene, toluene or xylene, to form an additive concentrate. These concentrates usually comprise about 0.1 to 80% by weight of the compositions of this invention and may contain, in addition, one or more other additives known in the art or described hereinabove. Concentrations such as 15%, 20%, 30% or 50% or higher may be employed. These concentrates are then added to lubricating oils at levels adequate to provide the required degree of performance.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

As mentioned hereinabove, and in the claims, the lubricating oil is present in a major amount and the various additives are used in minor amounts. A minor amount is less than 50 percent by weight of the total composition, whereas a major amount is more than 50 percent by weight of the composition. Thus, for example, 5, 10, 30 or 40 percent are minor amounts, while 51, 60, 70, 90, etc. percent are major amounts.

The lubricating compositions of this invention are illustrated by the examples in the following Table I. The lubricating compositions are prepared by combining the specified ingredients, individually or from concentrates, in the indicated amounts and oil of lubricating viscosity to make the total 100 parts by weight. All parts and percentages are by weight of the total composition unless otherwise indicated. Unless indicated otherwise, the amount of each listed additive is that of the neat additive, free of oil or other diluent. These examples are presented for illustrative purposes only, and are not intended to limit the scope of this invention.

TABLE I

A series of SAE 5W-30 lubricating oil compositions are prepared by making up a master blend comprising a mineral oil of lubricating viscosity (Sun Oil Co. stocks), 2.56 percent styrene-alkyl maleate copolymer, 1.96 percent of a reaction product of ethylene polyamines with polyisobutenyl succinic anhydride, 0.95 percent of overbased metal sulfonates, 1.60 percent of zinc dialkyl phosphorodithioates and 5 ppm of a silicone antifoam, and adding thereto the indicated amounts of the following components to prepare 100 parts by weight of blend:

<u>Example</u>	<u>Component-Product of Example:</u>	<u>Parts by weight</u>
A	3	1
B	4	1
C	15	1
D	14	3.3

Table II

Two blends (SAE 10W-30) are prepared, each blend comprising mineral oil (Exxon stocks), 0.53 percent of styrene-isoprene copolymer, 0.12 percent styrene-alkyl maleate copolymer, 1.72 parts of a reaction product of ethylene polyamine with polyisobutenyl succinic anhydride, 0.10 percent of fatty acid amide, 1.03 percent of zinc dialkyl phosphorodithioates, 0.20 percent of a sulfurized Diels-Alder adduct, 0.09 percent alkylated diphenyl amine, 0.87 percent of overbased metal sulfonates, 6 ppm of a silicone antifoam and the indicated amount of polyester:

<u>Example</u>	<u>Component-Product of Example:</u>	<u>Parts by weight per 100 parts blend</u>
E	3	0.50
F	3	0.85

Table IIIEngine Lubricating Oil Compositions

Component	Parts by Weight	
	Example G	Example H
Oil	Exxon 10W-30*	Sun 10W-30*
Styrene-isoprene copolymer	0.53	
Reaction product:ethylene polyamine and polyisobutenyl succinic anhydride	1.72	1.13
Styrene-alkyl maleate copolymer	0.12	
Reaction product:ethylene polyamine-polyol-polyisobutenyl succinic anhydride		1.38
Zinc dialkyl phosphorodithioates	1.03	1.16
Overbased metal sulfonates		1.08
Sulfurized Diels-Alder Adduct	0.20	0.20
Alkylated diphenyl amine	0.09	
Silicone antifoam	6 ppm	
Sulfurized alkyl phenol		0.69
Ethylene-propylene copolymer, diene modified		0.75
Polymer of alkylated unsaturated dicarboxylic acid vinyl carboxylate and vinyl alkyl ether		0.14
Product of Example 3	0.50	
Product of Example 5		1.0

*Mineral oil of lubricating viscosity in amount sufficient to bring total blend to 100 parts by weight.

The fuel consumption of internal combustion engines is reduced when the engines are lubricated with the compositions of this invention. This can be shown by the Friction Horsepower Test, in which an engine is driven by a motoring-absorbing dynamometer at controlled temperatures while engine r.p.m. and torque are measured by a digital tachometer and a precision dial manometer, respectively. Friction horsepower, as calculated from these values, is roughly proportional to fuel consumed in an operating engine. Lubricants which reduce friction horsepower levels in test engines can increase vehicle fuel economy.

Lubricating oil compositions E, F and G are evaluated using the above-described Friction Horsepower Test employing 3.8 liter Buick V-6 engines. These compositions show improvements over baselines of 8%, 10.2%

and 13%, respectively.

Baseline lubricating compositions are essentially the same as Examples E, F and G except that they do not contain the additives of this invention.

The instant invention is shown and described herein in what is considered to be the most practical, and the preferred embodiments. It is recognized, however, that departures may be made therefrom which are within the scope of the invention, and that obvious modifications will occur to one skilled in the art upon reading this disclosure.

Claims

1. A lubricating composition comprising a major amount of a mineral oil of lubricating viscosity and a minor amount of at least one polysuccinate ester having a molecular weight between 1000 and 4000, and which is substantially free of cycloaliphatic groups, and wherein succinic groups of the polysuccinate ester contain alkyl or alkenyl substituents having from 4 to 28 carbon atoms.
2. A composition according to claim 1 wherein the substituents contain 12 to 24 carbon atoms.
3. A composition according to claim 1 or claim 2 wherein the succinate esters are glycol esters, glycerol esters, pentaerythritol esters, or neo-diol esters.
4. A composition according to any preceding claim wherein the polyester has an acid number as determined by ASTM D-974 of from 0 to 60.
5. A composition according to any preceding claim wherein the polysuccinate ester contains terminal carboxylic acid groups.
6. A composition according to claim 5 wherein at least 50% of the terminal carboxylic acid groups are converted to amido groups, ester groups, salts, or mixtures thereof.
7. A composition according to any preceding claim wherein the polyester has a molecular weight between 2000 and 4000 and an acid number as determined by ASTM D-974 of from 10 to 20.
8. A lubricating composition according to claim 1 wherein the polysuccinate ester is prepared by the condensation reaction of
 - (A) at least one alkyl or alkenyl substituted succinic acid or anhydride, wherein the alkyl or alkenyl substituent contains from 4 to 28 carbon atoms, with
 - (B) at least one open-chain aliphatic compound having at least two OH groups, wherein the ratio of reactant A to reactant B is from one succinic group:1.8 OH groups to 1 succinic group:4 OH groups.
9. A composition according to claim 8 wherein the substituent contains from 12 to 24 carbon atoms.
10. A composition according to claim 8 or claim 9 wherein the substituent on (A) is a substantially linear group.
11. A composition according to any one of claims 8 to 10 wherein (B) contains an average of from 2 to 4 OH groups.
12. A composition according to any one of claims 8 to 11 wherein (B) is at least one of ethylene glycol, neopentylene glycol, glycerol, and pentaerythritol or mixtures thereof.
13. A composition according to any one of claims 8 to 11 wherein (B) is a fatty acid monoester of glycerol or a dihydroxypolyalkoxyalkane.
14. A composition according to any one of claims 8 to 13 wherein (A) is a succinic anhydride.
15. A composition according to any one of claims 8 to 14 wherein the ratio of reactant (A) to reactant (B) is from 1 succinic group: 2 OH groups to 1 succinic group: 2.4 OH groups.
16. A composition according to any one of claims 8 to 15 wherein the polyester is capped by reacting terminal



and 13%, respectively.

Baseline lubricating compositions are essentially the same as Examples E, F and G except that they do not contain the additives of this invention.

The instant invention is shown and described herein in what is considered to be the most practical, and the preferred embodiments. It is recognized, however, that departures may be made therefrom which are within the scope of the invention, and that obvious modifications will occur to one skilled in the art upon reading this disclosure.

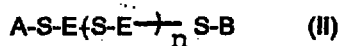
Claims

1. A lubricating composition comprising a major amount of a mineral oil of lubricating viscosity and a minor amount of at least one polysuccinate ester having a molecular weight between 1000 and 4000, and which is substantially free of cycloaliphatic groups, and wherein succinic groups of the polysuccinate ester contain alkyl or alkenyl substituents having from 4 to 28 carbon atoms.
2. A composition according to claim 1 wherein the substituents contain 12 to 24 carbon atoms.
3. A composition according to claim 1 or claim 2 wherein the succinate esters are glycol esters, glycerol esters, pentaerythritol esters, or neo-diol esters.
4. A composition according to any preceding claim wherein the polyester has an acid number as determined by ASTM D-974 of from 0 to 60.
5. A composition according to any preceding claim wherein the polysuccinate ester contains terminal carboxylic acid groups.
6. A composition according to claim 5 wherein at least 50% of the terminal carboxylic acid groups are converted to amido groups, ester groups, salts, or mixtures thereof.
7. A composition according to any preceding claim wherein the polyester has a molecular weight between 2000 and 4000 and an acid number as determined by ASTM D-974 of from 10 to 20.
8. A lubricating composition according to claim 1 wherein the polysuccinate ester is prepared by the condensation reaction of
 - (A) at least one alkyl or alkenyl substituted succinic acid or anhydride, wherein the alkyl or alkenyl substituent contains from 4 to 28 carbon atoms, with
 - (B) at least one open-chain aliphatic compound having at least two OH groups, wherein the ratio of reactant A to reactant B is from one succinic group:1.8 OH groups to 1 succinic group:4 OH groups.
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10. A composition according to claim 8 or claim 9 wherein the substituent on (A) is a substantially linear group.
11. A composition according to any one of claims 8 to 10 wherein (B) contains an average of from 2 to 4 OH groups.
12. A composition according to any one of claims 8 to 11 wherein (B) is at least one of ethylene glycol, neopentylene glycol, glycerol, and pentaerythritol or mixtures thereof.
13. A composition according to any one of claims 8 to 11 wherein (B) is a fatty acid monoester of glycerol or a dihydroxypolyalkoxyalkane.
14. A composition according to any one of claims 8 to 13 wherein (A) is a succinic anhydride.
15. A composition according to any one of claims 8 to 14 wherein the ratio of reactant (A) to reactant (B) is from 1 succinic group: 2 OH groups to 1 succinic group: 2.4 OH groups.
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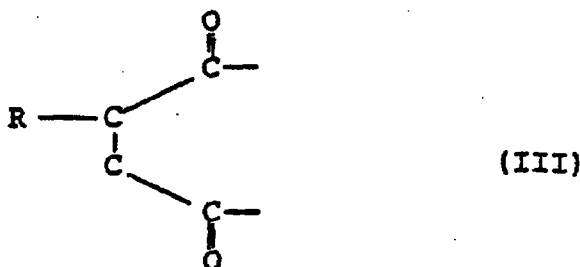


carboxylic acid groups with a monohydric alcohol, an isocyanate, a diol, a metal-containing reagent, or an amine.

17. A composition according to any one of claims 8 to 16 wherein the polyester has a molecular weight of 1400 to 4000.
18. A composition according to claim 17 wherein the polyester has a molecular weight from 2000 to 3000.
19. A composition according to any one of claims 8 to 18 wherein the polyester has an acid number as determined by ASTM D-974 of 0 to 60.
20. A composition according to any one of claims 8 to 16 wherein the polyester has a molecular weight between 2000 and 4000 and an acid number as determined by ASTM D-974 of from 10 to 20.
21. A lubricating composition according to claim 1 wherein the polysuccinate ester is prepared by the condensation reaction of
 - (A) at least one alkyl or alkenyl substituted succinic acid or anhydride, wherein the alkyl group contains from 4 to 28 carbon atoms, with
 - (C) at least one epoxide.
22. A composition according to claim 21 wherein the epoxide (C) is an alpha-olefin epoxide containing from 2 to 24 carbon atoms.
23. A composition according to claim 22 wherein the epoxide (C) contains from 8 to 18 carbon atoms.
24. A composition according to any one of claims 21 to 23 wherein the molar ratio of (A):(C) in the reaction mixture is between 0.8:1.2 and 1.2:0.8.
25. A composition according to any one of claims 21 to 24 wherein the substituent contains from 12 to 24 carbon atoms.
26. A composition according to any one of claims 21 to 25 wherein at least 50% of terminal carboxylic acid groups presents in the polyester are converted to amido groups, ester groups, salts or mixtures thereof.
27. A polysuccinate ester of the formula



wherein n is a number between 1 and 8,
each S is a group of the formula



wherein R is an alkyl or alkenyl group having from 4 to 28 carbon atoms, and
each E is a group of the formula



wherein R' is selected from

alkylene groups having from 2 to 28 carbon atoms,
hydroxy substituted alkylene groups having from 2 to 28 carbons, and containing from one to 6 hydroxy groups, with the proviso that the number of hydroxy groups does not exceed the unsatisfied valences of R', and



succinate ester substituted alkylene groups, and wherein a is a number of from 1 to 8, wherein each A and each B is independently

-OH,

-OR², wherein R² is an alkyl group containing from 1 to 28 carbons,

-O(R'O)_bH, wherein R' is an alkylene group containing from 2 to 28 carbon atoms, and b is a number ranging from 1 to 8, and

-NR³, wherein each R³ is independently H or an alkyl group having from 1 to 18 carbon atoms, with the proviso that at least one of A or B is not -OH, or, when A or B is -OH, a salt may be formed by reaction with a basic metal containing reagent, ammonia or an amine, and which polysuccinate ester has a molecular weight between 1000 and 4000.

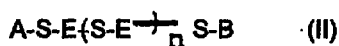
28. An ester of claim 27 wherein R contains from 12 to 20 carbon atoms, and n is a number between 1 and 4.
29. An ester according to claim 27 or 28 wherein each R' is independently alkylene of from 2 to 16 carbon atoms or hydroxy substituted alkylene having from 1 to 3 hydroxy groups.
30. A lubricating composition comprising a major amount of a mineral oil of lubricating viscosity and a minor amount of a polysuccinate ester according to any one of claims 27 to 29.
31. A composition according to any one of claims 1 to 26 or 30 wherein the composition comprises from 0.10% to 35% by weight of the polysuccinate ester.
32. A method for reducing the internal friction of an internal combustion engine which comprises lubricating the internal parts of said engine with a lubricating composition of any one of claims 1 to 26, 30 or 31.

Patentansprüche

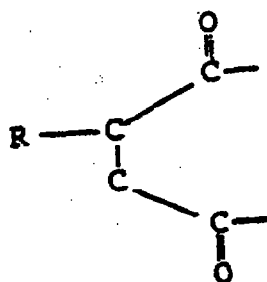
1. Schmiermittel, umfassend eine größere Menge eines Mineralöls mit Schmierviskosität und eine kleinere Menge von mindestens einem Polybernsteinsäureester der ein Molekulargewicht zwischen 1000 und 4000 aufweist, und der im wesentlichen frei von cycloaliphatischen Gruppen ist und wobei die Bernsteinsäuregruppen des Polybernsteinsäureesters Alkyl- oder Alkenylsubstituenten mit 4 bis 28 Kohlenstoffatomen enthalten.
2. Mittel nach Anspruch 1, wobei die Substituenten 12 bis 24 Kohlenstoffatome enthalten.
3. Mittel nach Anspruch 1 oder 2, wobei die Bernsteinsäureester Glycolester, Glycerinester, Pentaerythritester oder Neodiolester sind.
4. Mittel nach einem der vorstehenden Ansprüche, wobei der Polyester eine nach ASTM D-974 bestimmte Säurezahl von 0 bis 60 aufweist.
5. Mittel nach einem der vorstehenden Ansprüche, wobei der Polybernsteinsäureester entständige Carbonsäuregruppen enthält.
6. Mittel nach Anspruch 5, wobei mindestens 50 % der endständigen Carbonsäuregruppen in Amidgruppen, Estergruppen, Salze oder Gemische davon umgewandelt werden.
7. Mittel nach einem der vorstehenden Ansprüche, wobei der Polyester ein Molekulargewicht zwischen 2000 und 4000 und eine nach ASTM D-974 bestimmte Säurezahl von 10 bis 20 aufweist.
8. Schmiermittel nach Anspruch 1, wobei der Polybernsteinsäureester hergestellt wird durch die Kondensationsreaktion von
 - (A) mindestens einer alkyl- oder alkenylsubstituierten Bernsteinsäure oder deren Anhydrid, wobei der Alkyl- oder Alkenylsubstituent 4 bis 28 Kohlenstoffatome enthält, mit
 - (B) mindestens einer offenkettigen aliphatischen Verbindung mit mindestens zwei OH-Gruppen, wobei das Verhältnis des Reaktanten A zu dem Reaktanten B von 1 Bernsteinsäuregruppe : 1,8 OH-Gruppen bis 1 Bernsteinsäuregruppe : 4 OH-Gruppen beträgt.



9. Mittel nach Anspruch 8, wobei der Substituent von 12 bis 24 Kohlenstoffatome enthält.
10. Mittel nach Anspruch 8 oder 9, wobei der Substituent an (A) ein im wesentlichen linearer Rest ist.
- 5 11. Mittel nach einem der Ansprüche 8 bis 10, wobei (B) durchschnittlich 2 bis 4 OH-Gruppen enthält.
12. Mittel nach einem der Ansprüche 8 bis 11, wobei (B) mindestens eines von Ethylenglykol, Neopentylenglykol, Glycerin, und Pentaerythrit oder Gemische davon ist.
- 10 13. Mittel nach einem der Ansprüche 8 bis 11, wobei (B) ein Fettsäuremonoester von Glycerin oder ein Dihydroxypolyalkoxyalkan ist.
14. Mittel nach einem der Ansprüche 8 bis 13, wobei (A) ein Bernsteinsäureanhydrid ist.
- 15 15. Mittel nach einem der Ansprüche 8 bis 14, wobei das Verhältnis von Reaktant (A) zu Reaktant (B) von 1 Bernsteinsäuregruppe : 2 OH-Gruppen bis 1 Bernsteinsäuregruppe : 2,4 OH-Gruppen beträgt.
16. Mittel nach einem der Ansprüche 8 bis 15, wobei der Polyester durch Umsetzen der endständigen Carbonsäuregruppen mit einem einwertigen Alkohol, einem Isocyanat, einem Diol, einem metallhaltigen Reagenz oder einem Amin mit einer Endgruppe versehen wird.
- 20 17. Mittel nach einem der Ansprüche 8 bis 16, wobei der Polyester ein Molekulargewicht von 1400 bis 4000 aufweist.
18. Mittel nach Anspruch 17, wobei der Polyester ein Molekulargewicht von 2000 bis 3000 aufweist.
- 25 19. Mittel nach einem der Ansprüche 8 bis 18, wobei der Polyester eine nach ASTM D-974 bestimmte Säurezahl von 0 bis 60 aufweist.
20. Mittel nach einem der Ansprüche 8 bis 16, wobei der Polyester ein Molekulargewicht zwischen 2000 und 4000 und eine nach ASTM D-974 bestimmte Säurezahl von 10 bis 20 aufweist.
- 30 21. Schmiermittel nach Anspruch 1, wobei der Polybernsteinsäureester hergestellt wird durch die Kondensationsreaktion von
 - (A) mindestens einer alkyl- oder alkenylsubstituierten Bernsteinsäure oder deren Anhydrid, wobei der Alkyl- oder Alkenylrest 4 bis 28 Kohlenstoffatome enthält, mit
 - 35 (C) mindestens einem Epoxid.
22. Mittel nach Anspruch 21, wobei das Epoxid (C) ein α -Olefinepoxid mit 2 bis 24 Kohlenstoffatomen ist.
23. Mittel nach Anspruch 22, wobei das Epoxid (C) 8 bis 18 Kohlenstoffatome enthält.
- 40 24. Mittel nach einem der Ansprüche 21 bis 23, wobei das molare Verhältnis von (A):(C) in dem Reaktionsgemisch zwischen 0,8:1,2 und 1,2:0,8 liegt.
25. Mittel nach einem der Ansprüche 21 bis 24, wobei der Substituent 12 bis 24 Kohlenstoffatome enthält.
- 45 26. Mittel nach einem der Ansprüche 21 bis 25, wobei mindestens 50 % der endständigen Carbonsäuregruppen in dem Polyester zu Amidgruppen, Estergruppen, Salzen oder Gemischen davon umgewandelt werden.
- 50 27. Polybernsteinsäureester der Formel



in der n eine Zahl zwischen 1 und 8 ist,
jedes S ein Rest der Formel



(III)

ist, in der R ein Alkyl- oder Alkenylrest mit 4 bis 28 Kohlenstoffatomen ist, und jedes E ein Rest der Formel



ist, in der R' ausgewählt ist aus

Alkylenresten mit 2 bis 28 Kohlenstoffatomen,

hydroxysubstituierten Alkylenresten mit 2 bis 28 Kohlenstoffatomen und 1 bis 6 Hydroxylgruppen, mit der Maßgabe, daß die Anzahl der Hydroxylgruppen nicht größer ist als die nicht-abgesättigten Valenzen von R', und Bernsteinsäureester-substituierten Alkylenresten, und wobei a eine Zahl von 1 bis 8 ist, wobei jedes A und jedes B unabhängig voneinander

-OH,

-OR², wobei R² ein Alkylrest mit 1 bis 28 Kohlenstoffatomen ist,

-O(R'O)_bH, wobei R' ein Alkylenrest mit 2 bis 28 Kohlenstoffatomen ist und b eine Zahl im Bereich von 1 bis 8 ist, und

-NR₂³ ist, wobei jedes R³ unabhängig voneinander ein Wasserstoffatom oder ein Alkylrest mit 1 bis 18 Kohlenstoffatomen ist, mit der Maßgabe, daß mindestens eines von A oder B kein -OH ist, oder, wenn A oder B -OH ist, ein Salz durch Umsetzung mit einem ein basisches Metall enthaltenen Reagenz, Ammoniak oder einem Amin hergestellt werden kann, und wobei der Polybernsteinsäureester ein Molekulargewicht zwischen 1000 und 4000 aufweist.

28. Ester nach Anspruch 27, wobei R von 12 bis 20 Kohlenstoffatome enthält und n eine Zahl zwischen 1 und 4 ist.

29. Ester nach Anspruch 27 oder 28, wobei jedes R' unabhängig voneinander ein Alkylenrest mit 2 bis 16 Kohlenstoffatomen oder ein hydroxysubstituierter Alkylenrest mit 1 bis 3 Hydroxylgruppen ist.

30. Schmiermittel, das eine größere Menge eines Mineralöls mit Schmierviskosität und eine kleinere Menge eines Polybernsteinsäureesters nach einem der Ansprüche 27 bis 29 enthält.

31. Mittel nach einem der Ansprüche 1 bis 26 oder 30, wobei das Mittel 0,10 bis 35 Gew.-% des Polybernsteinsäureesters umfaßt.

32. Verfahren zur Verminderung der inneren Reibung eines Innenverbrennungsmotors, das das Schmieren der inneren Teile des Motors mit einem Schmiermittel nach einem der Ansprüche 1 bis 26, 30 oder 31 umfaßt.

Revendications

1. Une composition lubrifiante comprenant une quantité majeure d'une huile minérale d'une viscosité lubrifiante et une quantité mineure d'au moins un ester polysuccinate ayant un poids moléculaire compris entre 1000 et 4000 et qui est substantiellement exempt de groupes cyclo-aliphatiques, et dans lequel les groupes succiniques de l'ester polysuccinate contiennent des substituants alcoyle ou alcényle ayant de 4 à 28 atomes de carbone.

2. Une composition selon la revendication 1, dans laquelle les substituants contiennent de 12 à 24 atomes de carbone.

3. Une composition selon la revendication 1 ou la revendication 2, dans laquelle les esters succinate sont



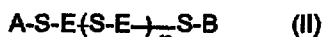
des esters de glycol, des esters de glycérol, des esters de penta-érythritol ou des esters de néo-diol.

4. Une composition selon l'une quelconque des revendications précédentes, dans laquelle le polyester a un indice d'acide tel que déterminé selon la norme ASTM D-974 compris entre 0 et 60.
5. Une composition selon l'une quelconque des revendications précédentes, dans laquelle l'ester polysuccinate contient des groupes acide carboxylique terminaux.
6. Une composition selon la revendication 5, dans laquelle au moins 50 % des groupes acide carboxylique terminaux sont transformés en groupes amido, groupes ester, sels ou leurs mélanges.
7. Une composition selon l'une quelconque des revendications précédentes, dans laquelle le polyester a un poids moléculaire compris entre 2000 et 4000 et un indice d'acide tel que déterminé selon la norme ASTM D-974 compris entre 10 et 20.
8. Une composition lubrifiante selon la revendication 1, dans laquelle l'ester polysuccinate est préparé par la réaction de condensation de
 - (A) au moins un acide ou anhydride alcoyl ou alcényl succinique, dans lequel le substituant alcoyle ou alcényle contient de 4 à 28 atomes de carbone, avec
 - (B) au moins un composé aliphatique à chaîne ouverte ayant au moins deux groupes OH,où le rapport du corps en réaction A au corps en réaction B est compris entre 1 groupe succinique pour 1,8 groupe OH et 1 groupe succinique pour 4 groupes OH.
9. Une composition selon la revendication 8, dans laquelle le substituant contient de 12 à 24 atomes de carbone.
10. Une composition selon la revendication 8 ou 9, dans laquelle le substituant sur (A) est un groupe substantiellement linéaire.
11. Une composition selon l'une quelconque des revendications 8 à 10, dans laquelle (B) contient une moyenne de 2 à 4 groupes OH.
12. Une composition selon l'une quelconque des revendications 8 à 11, dans laquelle (B) est au moins un composé choisi parmi l'éthylène glycol, le néopentylène glycol, le glycérol et le penta-érythritol ou leurs mélanges.
13. Une composition selon l'une quelconque des revendications 8 à 11, dans laquelle (B) est un monoester d'acide gras de glycérol ou un dihydroxypolyalcoxyalcane.
14. Une composition selon l'une quelconque des revendications 8 à 11, dans laquelle (A) est un anhydride succinique.
15. Une composition selon l'une quelconque des revendications 8 à 14, dans laquelle le rapport du corps en réaction (A) au corps en réaction (B) est compris entre 1 groupe succinique pour 2 groupes OH et 1 groupe succinique pour 2,4 groupes OH.
16. Une composition selon l'une quelconque des revendications 8 à 15, dans laquelle le polyester est coiffé par réaction des groupes acide carboxylique terminaux avec un alcool monohydrique, un isocyanate, un diol, un réactif contenant un métal ou une amine.
17. Une composition selon l'une quelconque des revendications 8 à 16, dans laquelle le polyester a un poids moléculaire de 1400 à 4000.
18. Une composition selon la revendication 17, dans laquelle le polyester a un poids moléculaire compris entre 2000 et 3000.
19. Une composition selon l'une quelconque des revendications 8 à 18, dans laquelle le polyester a un indice d'acide tel que déterminé selon la norme ASTM D-974 de 0 à 60.
20. Une composition selon l'une quelconque des revendications 8 à 16, dans laquelle le polyester a un poids moléculaire compris entre 2000 et 4000 et un indice d'acide tel que déterminé selon la norme ASTM D-

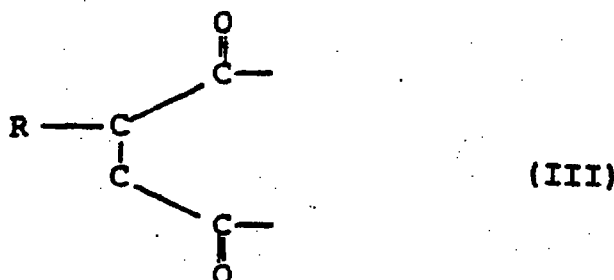


974 compris entre 10 et 20.

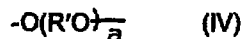
21. Une composition lubrifiante selon la revendication 1, dans laquelle l'ester polysuccinate est préparé par la réaction de condensation de
- (A) au moins un acide alcoyl ou alcényl succinique, dans lequel le groupe alcoyle contient de 4 à 28 atomes de carbone, avec
- (C) au moins un époxyde.
22. Une composition selon la revendication 21, dans laquelle l'époxyde (C) est un époxyde d'alpha-oléfine contenant de 2 à 24 atomes de carbone.
23. Une composition selon la revendication 22, dans laquelle l'époxyde (C) contient de 8 à 18 atomes de carbone.
24. Une composition selon l'une quelconque des revendications 21 à 23, dans laquelle le rapport molaire de (A) à (C) dans le mélange de réaction est compris entre 0,8:1,2 et 1,2:0,8.
25. Une composition selon l'une quelconque des revendications 21 à 24, dans laquelle le substituant contient de 12 à 24 atomes de carbone.
26. Une composition selon l'une quelconque des revendications 21 à 25, dans laquelle au moins 50 % des groupes acide carboxylique terminaux présents dans le polyester sont transformés en groupes amido, groupes ester, sels ou leurs mélanges.
27. Un ester polysuccinate de la formule



dans laquelle n est un nombre compris entre 1 et 8,
chaque S est un groupe de la formule



dans laquelle R est un groupe alcoyle ou alcényle ayant de 4 à 8 atomes de carbone, et
chaque E est un groupe de la formule



où R' est choisi parmi

des groupes alcoylène ayant de 2 à 28 atomes de carbone,
des groupes alcoylène hydroxylés ayant de 2 à 28 atomes de carbone et contenant de 1 à 6 groupes hydroxy, avec la condition que le nombre de groupes hydroxy ne dépasse pas le nombre de valences non satisfaites de R', et

des groupes alcoylène substitués par des groupes ester succinate, et
a est un nombre de 1 à 8,

où chaque A et chaque B sont choisis indépendamment parmi

-OH,
-OR², où R² est un groupe alcoyle contenant de 1 à 28 atomes de carbone,
-O(R'O)_bH, où R' est un groupe alcoylène contenant de 2 à 28 atomes de carbone, et b est un nombre allant de 1 à 8, et
-NR³, où chaque R³ est indépendamment H ou un groupe alcoyle ayant de 1 à 18 atomes de carbone, avec la condition qu'au moins un de A ou B n'est pas -OH, ou, quand A ou B est -OH, un sel peut



être formé par réaction avec un réactif basique contenant un métal, l'ammoniac ou une amine, et l'ester polysuccinate a un poids moléculaire compris entre 1000 et 4000.

28. Un ester selon la revendication 27, dans lequel R contient de 12 à 20 atomes de carbone et n est un nombre compris entre 1 et 4.

29. Un ester selon la revendication 27 ou 28, dans lequel chaque R' indépendamment est un groupe alcoylène ayant de 2 à 16 atomes de carbone ou un groupe alcoylène hydroxylé ayant de 1 à 3 groupes hydroxy.

30. Une composition lubrifiante comprenant une quantité majeure d'une huile minérale d'une viscosité lubrifiante et une quantité mineure d'un ester polysuccinate selon l'une quelconque des revendications 27 à 29.

31. Une composition selon l'une quelconque des revendications 1 à 26 ou 30, la composition comprenant de 0,10 % à 35 % en poids de l'ester polysuccinate.

32. Une méthode pour réduire le frottement interne d'un moteur à combustion interne, qui comprend le graissage des parties internes de ce moteur avec une composition lubrifiante selon l'une quelconque des revendications 1 à 26, 30 ou 31.