

BIODEGRADABLE BRANCHED SYNTHETIC ESTER BASE STOCKS AND LUBRICANTS FORMED THEREFROM

5 The present invention relates generally to the use of branched synthetic esters to improve the cold-flow properties and dispersant solubility of biodegradable lubricant base stocks without loss of biodegradation or lubrication. At least 60% biodegradation (as measured by the Modified Sturm test) can be achieved with branching along the chains of the acyl and/or alcohol portions of the ester. These branched synthetic esters are particularly useful in the formation of biodegradable lubricants in two-cycle engine oils, catapult oils, hydraulic fluids, drilling fluids, water turbine oils, greases, compressor oils, and other industrial and engine applications where biodegradability is needed or desired.

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BACKGROUND OF THE INVENTION

 The interest in developing biodegradable lubricants for use in applications which result in the dispersion of such lubricants into waterways, such as rivers, oceans and lakes, has generated substantial interest by both the environmental community and lubricant manufacturers. The synthesis of a lubricant which maintains its cold-flow properties and additive solubility without loss of biodegradation or lubrication would be highly desirable.

25 Base stocks for biodegradable lubricant applications (e.g., two-cycle engine oils, catapult oils, hydraulic fluids, drilling fluids, water turbine oils, greases and compressor oils) should typically meet five criteria: (1) solubility with dispersants and other additives such as polyamides; (2) good cold flow properties (such as, less than -40°C pour point; less than 7500 cps at -25°C); (3) sufficient biodegradability to off-set the low biodegradability of any dispersants and/or other additives to the formulated lubricant; (4) good lubricity without the aid of wear additives; and (5) high flash point (greater than 260°C, flash and fire points by COC (Cleveland Open Cup) as measured by ASTM test number D-92).

35 The Organization for Economic Cooperation and Development (OECD) issued draft test guidelines for degradation and accumulation testing in December

1979. The Expert Group recommended that the following tests should be used to determine the "ready biodegradability" of organic chemicals: Modified OECD Screening Test, Modified MITI Test (I), Closed Bottle Test, Modified Sturm Test and the Modified AFNOR Test. The Group also recommended that the following

5 "pass levels" of biodegradation, obtained within 28 days, may be regarded as good evidence of "ready biodegradability": (Dissolved Organic Carbon (DOC)) 70%; (Biological Oxygen Demand (BOD)) 60%; (Total Organic Carbon (TOD)) 60%; (CO₂) 60%; and (DOC) 70%, respectively, for the tests listed above. Therefore, the "pass level" of biodegradation, obtained within 28 days, using the Modified

10 Sturm Test is at least (CO₂) 60%.

Since the main purpose in setting the test duration at 28 days was to allow sufficient time for adaptation of the micro-organisms to the chemical (lag phase), this should not allow compounds which degrade slowly, after a relatively short

15 adaptation period, to pass the test. A check on the rate of biodegradation therefore should be made. The "pass level" of biodegradation (60%) must be reached within 10 days of the start of biodegradation. Biodegradation is considered to have begun when 10% of the theoretical CO₂ has evolved. That is, a readily biodegradable fluid should have at least a 60% yield of CO₂ within 28 days,

20 and this level must be reached within 10 days of biodegradation exceeding 10%. This is known as the "10-Day Window."

The OECD guideline for testing the "ready biodegradability" of chemicals under the Modified Sturm test (OECD 301B, adopted May 12, 1981, and which is

25 incorporated herein by reference) involves the measurement of the amount of CO₂ produced by the test compound which is measured and expressed as a percent of the theoretical CO₂ (TCO₂) it should have produced calculated from the carbon content of the test compound. Biodegradability is therefore expressed as a percentage of TCO₂. The Modified Sturm test is run by spiking a chemically

30 defined liquid medium, essentially free of other organic carbon sources, with the test material and inoculated with sewage micro-organisms. The CO₂ released is trapped as BaCO₃. After reference to suitable blank controls, the total amount of CO₂ produced by the test compound is determined for the test period and calculated as the percentage of total CO₂ that the test material could have

35 theoretically produced based on carbon composition. See G. van der Waal and D.

Kenbeek, "Testing, Application, and Future Development of Environmentally Friendly Ester Based Fluids", Journal of Synthetic Lubrication, Vol. 10, Issue No. 1, April 1993, pp. 67-83, which is incorporated herein by reference.

5 One base stock in current use today is rapeseed oil (i.e., a triglyceride of fatty acids, e.g., 7 % saturated C₁₂ to C₁₈ acids, 50% oleic acid, 36% linoleic acid and 7% linolenic acid, having the following properties: a viscosity at 40°C of 47.8 cSt, a pour point of 0°C, a flash point of 162°C and a biodegradability of 85% by the Modified Sturm test. Although it has very good biodegradability, its use in
10 biodegradable lubricant applications is limited due to its poor low temperature properties and poor stability.

 Unless they are sufficiently low in molecular weight, esters synthesized from both linear acids and linear alcohols tend to have poor low temperature
15 properties. Even when synthesized from linear acids and highly branched alcohols, such as polyol esters of linear acids, high viscosity esters with good low temperature properties can be difficult to achieve. In addition, pentaerythritol esters of linear acids exhibit poor solubility with dispersants such as polyamides, and trimethylolpropane esters of low molecular weight (i.e., having a carbon
20 number less than 14) linear acids do not provide sufficient lubricity. This lower quality of lubricity is also seen with adipate esters of branched alcohols. Since low molecular weight linear esters also have low viscosities, some degree of branching is required to build viscosity while maintaining good cold flow properties. When both the alcohol and acid portions of the ester are highly branched, however, such
25 as with the case of polyol esters of highly branched oxo acids, the resulting molecule tends to exhibit poor biodegradation as measured by the Modified Sturm test (OECD Test No. 301B).

 In an article by Randles and Wright, "Environmentally Considerate Ester
30 Lubricants for the Automotive and Engineering Industries", Journal of Synthetic Lubrication, Vol. 9-2, pp. 145-161, it was stated that the main features which slow or reduce microbial breakdown are the extent of branching, which reduces β -oxidation, and the degree to which ester hydrolysis is inhibited. The negative effect on biodegradability due to branching along the carbon chain is further
35 discussed in a book by R.D. Swisher, "Surfactant Biodegradation", Marcel

Dekker, Inc., Second Edition, 1987, pp. 415-417. In his book, Swisher stated that "The results clearly showed increased resistance to biodegradation with increased branching... Although the effect of a single methyl branch in an otherwise linear molecule is barely noticeable, increased resistance [to biodegradation] with increased branching is generally observed, and resistance becomes exceptionally great when quaternary branching occurs at all chain ends in the molecule." The negative effect of alkyl branching on biodegradability was also discussed in an article by N.S. Battersby, S.E. Pack, and R.J. Watkinson, "A Correlation Between the Biodegradability of Oil Products in the CEC-L-33-T-82 and Modified Sturm Tests", Chemosphere, 24(12), pp. 1989-2000 (1992).

Initially, the poor biodegradation of branched polyol esters was believed to be a consequence of the branching and, to a lesser extent, to the insolubility of the molecule in water. However, recent work by the present inventors has shown that the non-biodegradability of these branched esters is more a function of steric hindrance than of the micro-organism's inability to breakdown the tertiary and quaternary carbons. Thus, by relieving the steric hindrance around the ester linkage(s), biodegradation can more readily occur with branched esters.

Branched synthetic polyol esters have been used extensively in non-biodegradable applications, such as refrigeration lubricant applications, and have proven to be quite effective if 3,5,5-trimethylhexanoic acid is incorporated into the molecule at 25 molar percent or greater. However, trimethylhexanoic acid is not biodegradable as determined by the Modified Sturm test (OECD 301B), and the incorporation of 3,5,5-trimethylhexanoic acid, even at 25 molar percent, would drastically lower the biodegradation of the polyol ester due to the quaternary carbons contained therein.

Likewise, incorporation of trialkyl acetic acids (i.e., neo acids) into a polyol ester produces very useful refrigeration lubricants. These acids do not, however, biodegrade as determined by the Modified Sturm test (OECD 301B) and cannot be used to produce polyol esters for biodegradable applications. Polyol esters of all branched acids can be used as refrigeration oils as well. However, they do not rapidly biodegrade as determined by the Modified Sturm Test (OECD 301B) and, therefore, are not desirable for use in biodegradable applications.

Although polyol esters made from purely linear C₅ and C₁₀ acids for refrigeration applications would be biodegradable under the Modified Sturm test, they would not work as a lubricant in hydraulic or two-cycle engine applications because the viscosities would be too low and wear additives would be needed. It is extremely difficult to develop a lubricant base stock which is capable of exhibiting all of the various properties required for biodegradable lubricant applications, i.e., high viscosity, low pour point, oxidative stability and biodegradability as measured by the Modified Sturm test.

U.S. Patent No. 4,826,633 (Carr et al.), which issued on May 2, 1989, discloses a synthetic ester lubricant base stock formed by reacting at least one of trimethylolpropane and monopentaerythritol with a mixture of aliphatic monocarboxylic acids. The mixture of acids includes straight-chain acids having from 5 to 10 carbon atoms and an iso-acid having from 6 to 10 carbon atoms, preferably iso-nonanoic acid (i.e., 3,5,5-trimethylhexanoic acid). This base stock is mixed with a conventional ester lubricant additive package to form a lubricant having a viscosity at 99°C (210°F) of at least 5.0 centistokes and a pour point of at least as low as -54°C (-65°F). This lubricant is particularly useful in gas turbine engines. The Carr et al. patent differs from the present invention for two reasons. Firstly, it preferably uses as its branched acid 3,5,5-trimethylhexanoic acid which contains a quaternary carbon in every acid molecule. The incorporation of quaternary carbons within the 3,5,5-trimethylhexanoic acid inhibits biodegradation of the polyol ester product. Also, since the lubricant according to Carr et al. exhibits high stability, as measured by a high pressure differential scanning calorimeter (HPDSC), i.e., about 35 to 65 minutes, the micro-organisms cannot pull them apart. Conversely, the lubricant according to the present invention is low in stability, i.e., it has a HPDSC reading of about 12-17 minutes. The lower stability allows the micro-organisms to attack the carbon-to-carbon bonds about the polyol structure and effectively cause the ester to biodegrade. One reason that the lubricant of the present invention is lower in stability is the fact that no more than 10% of the branched acids used to form the lubricant's ester base stock contain a quaternary carbon.

Therefore, the present inventors have discovered that highly biodegradable lubricants using biodegradable base stocks with good cold flow properties, good

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solubility with dispersants, and good lubricity can be achieved by incorporating branched acids into the ester molecule. The branched acids used in accordance with the present invention are needed to build viscosity and the multiple isomers in these acids are helpful in attaining low temperature properties. That is, the
5 branched acids allow the chemist to build viscosity without increasing molecular weight. Furthermore, branched biodegradable lubricants provide the following cumulative advantages over all linear biodegradable lubricants: (1) decreased pour point; (2) increased solubilities of other additives; (3) increased
detergency/dispersancy of the lubricant oil; and (4) increased oxidative stability in
10 hydraulic fluid and catapult oil applications.

The data compiled by the present inventors and set forth in the examples to follow show that all of the above listed properties can be best met with biodegradable lubricants formulated with biodegradable synthetic ester base stocks
15 which incorporate both highly branched acids and linear acids.

SUMMARY OF THE INVENTION

A biodegradable synthetic base stock which preferably comprises the
20 reaction product of: a branched or linear alcohol having the general formula $R(OH)_n$, wherein R is an aliphatic or cyclo-aliphatic group having from about 2 to 20 carbon atoms (preferably an alkyl) and n is at least 2 and up to about 10; and mixed acids comprising about 30 to 80 molar %, more preferably about 35 to 55 mole %, of a linear acid having a carbon number (i.e., carbon number means the
25 total number of carbon atoms in either the acid or alcohol as the case may be) in the range between about C_3 to C_{12} , more preferably about C_7 to C_{10} ; and about 20 to 70 molar %, more preferably about 35 to 55 mole %, of at least one branched acid having a carbon number in the range between about C_3 to C_{13} , more preferably about C_7 to C_{10} ; wherein the ester exhibits the following properties: at
30 least 60% biodegradation in 28 days as measured by the Modified Sturm test; a pour point of less than -25°C ; and a viscosity of less than 7500 cps at -25°C .

In the most preferred embodiment, it is desirable to have a branched acid comprising multiple isomers, preferably more than 3 isomers, most preferably more
35 than 5 isomers. The linear acid is preferably an alkyl mono- or di- carboxylic acid

having the general formula RCOOH , wherein R is an n-alkyl having between about 4 to 11 carbon atoms, more preferably between about 7 to 10 carbon atoms. It is also preferable that no more than 10% of the branched acids used to form the biodegradable synthetic ester base stock contain a quaternary carbon.

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These biodegradable synthetic base stocks are particularly useful in the formulation of biodegradable lubricants, such as, two-cycle engine oils, biodegradable catapult oils, biodegradable hydraulic fluids, biodegradable drilling fluids, biodegradable water turbine oils, biodegradable greases, biodegradable, compressor oils, functional fluids and other industrial and engine applications where biodegradability is needed or desired.

The formulated biodegradable lubricants according to the present invention preferably comprise about 60-99 % by weight of at least one biodegradable lubricant synthetic base stock discussed above, about 1 to 20 % by weight lubricant additive package, and about 0 to 20 % of a solvent.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

The branched synthetic ester base stock used in the formulation of various biodegradable lubricants and oils in accordance with the present invention is preferably formed from the reaction product of technical grade pentaerythritol, which comprises between about 86-92% mono-pentaerythritol, 6-12% di-pentaerythritol and 1-3% tri-pentaerythritol, with approximately 30-70 molar C_8 and C_{10} linear acids ("C810" linear acids) and approximately 30-70 molar % iso- C_8 (e.g., Cekanoic 8) branched acids.

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Neopentyl glycol (NPG) can be totally esterified with 2-ethylhexanoic acid or an iso- C_8 acid and still maintain about 90% biodegradation as measured by the Modified Sturm test. After two branched acids have been added to a branched polyol, the ester linkages begin to become crowded around the quaternary carbon of the branched alcohol. Additional branched acids added to the branched alcohol begin to lower the biodegradation of the molecule such that by the fourth addition of a branched acid to the branched alcohol, the biodegradation of the resulting

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molecule drops from about 80% to less than 15% biodegradation as measured by the Modified Sturm test.

Introduction of linear acids into the molecule relieves the steric crowding around the quaternary carbon of the branched alcohol. Thus, by having two
5 branched acids and two linear acids on pentaerythritol, for example, the enzymes have access to the ester linkages, and the first stage of biodegradation, i.e., the hydrolysis of the ester, can occur. In each of the pentaerythritol esters, the hydroxyl groups are esterified with the various branched and linear acids.

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ALCOHOLS

Among the alcohols which can be reacted with the branched and linear acids of the present invention are, by way of example, polyols (i.e., polyhydroxyl compounds) represented by the general formula:

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wherein R is any aliphatic or cyclo-aliphatic hydrocarbyl group (preferably an alkyl) and n is at least 2. The hydrocarbyl group may contain from about 2 to about 20 or more carbon atoms, and the hydrocarbyl group may also contain substituents such as chlorine, nitrogen and/or oxygen atoms. The polyhydroxyl
20 compounds generally will contain from about 2 to about 10 hydroxyl groups and more preferably from about 2 to about 6 hydroxy groups. The polyhydroxy compound may contain one or more oxyalkylene groups and, thus, the polyhydroxy compounds include compounds such as polyetherpolyols. The number of carbon atoms (i.e., carbon number) and number of hydroxy groups (i.e.,
25 hydroxyl number) contained in the polyhydroxy compound used to form the carboxylic esters may vary over a wide range.

The following alcohols are particularly useful as polyols: neopentyl glycol, 2,2-dimethylol butane, trimethylol ethane, trimethylol propane, trimethylol butane,
30 mono-pentaerythritol, technical grade pentaerythritol, di-pentaerythritol, ethylene glycol, propylene glycol and polyalkylene glycols (e.g., polyethylene glycols, polypropylene glycols, polybutylene glycols, etc., and blends thereof such as a polymerized mixture of ethylene glycol and propylene glycol).

The preferred branched or linear alcohols are selected from the group consisting of: technical grade pentaerythritol, mono-pentaerythritol, di-pentaerythritol, neopentylglycol, trimethylol propane, trimethylol ethane and propylene glycol, 1,4-butanediol, sorbitol and the like, and 2-methylpropanediol.

- 5 The most preferred alcohol is technical grade (i.e., 88% mono, 10% di and 1-2% tri) pentaerythritol.

BRANCHED ACIDS

- 10 The branched acid is preferably a mono-carboxylic acid which has a carbon number in the range between about C₅ to C₁₃, more preferably about C₇ to C₁₀ wherein methyl branches are preferred. The preferred branched acids are those wherein less than or equal to 10% of the branched acids contain a quaternary carbon. The mono-carboxylic acid is at least one acid selected from the group consisting of: 2-ethylhexanoic acids, isoheptanoic acids, iso-octanoic acids, iso-
- 15 nonanoic acids, iso-decanoic acids, and α -branched acids. The most preferred branched acid is iso-octanoic acids, e.g., C₈ acid.

It is desirable to have a branched acid comprising multiple isomers, preferably more than 3 isomers, most preferably more than 5 isomers.

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LINEAR ACIDS

- The preferred mono- and/or di-carboxylic linear acids are any linear, saturated alkyl carboxylic acids having a carbon number in the range between about 5 to 12, preferably 7 to 10. The most preferred linear acids are mono-
- 25 carboxylic acids.

- Some examples of linear acids include n-heptanoic, n-octanoic, n-decanoic and n-nonanoic acids. Selected diacids include adipic, azelaic, sebacic and dodecanedioic acids. For the purpose of modifying the viscosity of the resultant
- 30 ester product, up to 20 wt.% of the total acid mixture can consist of linear diacids.

BIODEGRADABLE LUBRICANTS

- The branched synthetic ester base stock can be used in the formulation of
- 35 biodegradable lubricants together with selected lubricant additives. The additives

listed below are typically used in such amounts so as to provide their normal attendant functions. Typical amounts for individual components are also set forth below. The preferred biodegradable lubricant contains approximately 80% or greater by weight of the basestock and 20% by weight of any combination of the following additives:

		(Broad) Wt. %	(Preferred) Wt. %
	Viscosity Index Improver	1-12	1-4
10	Corrosion Inhibitor	0.01-3	0.01-1.5
	Oxidation Inhibitor	0.01-5	0.01-1.5
	Dispersant	0.1-10	0.1-5
	Lube Oil Flow Improver	0.01-2	0.01-1.5
	Detergents and Rust Inhibitors	0.01-6	0.01-3
15	Pour Point Depressant	0.01-1.5	0.01-1.5
	Antifoaming Agents	0.001-0.1	0.001-0.01
	Antiwear Agents	0.001-5	0.001-1.5
	Seal Swellant	0.1-8	0.1-4
	Friction Modifiers	0.01-3	0.01-1.5
20	Biodegradable Synthetic Ester Base Stock	≥80%	≥80%

When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the dispersant (in concentrated amounts hereinabove described), together with one or more of the other additives (concentrate when constituting an additive mixture being referred to herein as an additive package) whereby several additives can be added simultaneously to the base stock to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the dispersant additive and optional additional additives in proper amounts to provide the desired concentration in the final formulation when the additive package is combined with a predetermined amount of base lubricant or base stock. Thus, the biodegradable lubricants according to the present invention can employ

typically up to about 20 wt.% of the additive package with the remainder being biodegradable ester base stock and/or a solvent.

All of the weight percents expressed herein (unless otherwise indicated) are based on active ingredient (A.I.) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the A.I. weight of each additive plus the weight of total oil or diluent.

Examples of the above additives for use in biodegradable lubricants are set forth in the following documents which are incorporated herein by reference: U.S. Patent No. 5,306,313 (Emert et al.), which issued on April 26, 1994; U.S. Patent No. 5,312,554 (Waddoups et al.), which issued on May 17, 1994; U.S. Patent No. 5,328,624 (Chung), which issued July 12, 1994; an article by Benfaremo and Liu, "Crankcase Engine Oil Additives", Lubrication, Texaco Inc., pp. 1 -7; and an article by Liston, "Engine Lubricant Additives What They are and How They Function", Lubrication Engineering, May 1992, pp. 389-397.

Viscosity modifiers impart high and low temperature operability to the lubricating oil and permit it to remain shear stable at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. These viscosity modifiers are generally high molecular weight hydrocarbon polymers including polyesters. The viscosity modifiers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties. Representative examples of suitable viscosity modifiers are any of the types known to the art including polyisobutylene, copolymers of ethylene and propylene, polymethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and vinyl compound, interpolymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline

earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulfurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as a terpene, a heavy petroleum fraction of a C₂ to C₆ olefin polymer such as polyisobutylene, with from 5 to 30 wt.% of a sulfide of phosphorus for 1/2 to 15 hours, at temperatures in the range of about 66 to about 316°C. Neutralization of the phosphosulfurized hydrocarbon may be effected in the manner taught in U.S. Patent No. 1,969,324.

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Oxidation inhibitors, or antioxidants, reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include alkaline earth metal salts of alkyl-phenolthioesters having preferably C₃ to C₁₂ alkyl side chains, e.g., calcium nonylphenol sulfide, barium octylphenylsulfide, dioctylphenylamine, phenylalphanaphthylamine, phosphosulfurized or sulfurized hydrocarbons, etc.

Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions such as automatic transmission fluids. Representative examples of suitable friction modifiers are fatty acid esters and amides, molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols, glycerol esters of dimerized fatty acids, alkane phosphonic acid salts, phosphonate with an oleamide, S-carboxyalkylene hydrocarbyl succinimide, N(hydroxyalkyl)alkenylsuccinamic acids or succinimides, di-(lower alkyl) phosphites and epoxides, and alkylene oxide adduct of phosphosulfurized N-(hydroxyalkyl)alkenyl succinimides. The most preferred friction modifiers are succinate esters, or metal salts thereof, of hydrocarbyl substituted succinic acids or anhydrides and thiobis-alkanols.

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Dispersants maintain oil insolubles, resulting from oxidation during use, in suspension in the fluid thus preventing sludge flocculation and precipitation or deposition on metal parts. Suitable dispersants include high molecular weight alkyl succinimides, the reaction product of oil-soluble polyisobutylene succinic

anhydride with ethylene amines such as tetraethylene pentamine and borated salts thereof.

Pour point depressants, otherwise known as lube oil flow improvers, lower the temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives which usually optimize the low temperature fluidity of the fluid are C₈ to C₁₈ dialkylfumarate vinyl acetate copolymers, polymethacrylates, and wax naphthalene. Foam control can be provided by an antifoamant of the polysiloxane type, e.g., silicone oil and polydimethyl siloxane.

Antiwear agents, as their name implies, reduce wear of metal parts. Representative of conventional antiwear agents are zinc dialkyldithiophosphate and zinc diaryldithiophosphate.

Antifoam agents are used for controlling foam in the lubricant. Foam control can be provided by an antifoamant of the high molecular weight dimethylsiloxanes and polyethers. Some examples of the polysiloxane type antifoamant are silicone oil and polydimethyl siloxane.

Detergents and metal rust inhibitors include the metal salts of sulphonic acids, alkyl phenols, sulfurized alkyl phenols, alkyl salicylates, naphthenates and other oil soluble mono- and di-carboxylic acids. Highly basic (viz. overbased) metal salts, such as highly basic alkaline earth metal sulfonates (especially Ca and Mg salts) are frequently used as detergents.

Seal swellants include mineral oils of the type that provoke swelling of engine seals, including aliphatic alcohols of 8 to 13 carbon atoms such as tridecyl alcohol, with a preferred seal swellant being characterized as an oil-soluble, saturated, aliphatic or aromatic hydrocarbon ester of from 10 to 60 carbon atoms and 2 to 4 linkages, e.g., dihexyl phthalate, as are described in U.S. Patent No. 3,974,081, which is incorporated by reference.

BIODEGRADABLE TWO-CYCLE ENGINE OILS

The branched synthetic ester base stock can be used in the formulation of biodegradable two-cycle engine oils together with selected lubricant additives. The preferred biodegradable two-cycle engine oil is typically formulated using the biodegradable synthetic ester base stock formed according to the present invention together with any conventional two-cycle engine oil additive package. The additives listed below are typically used in such amounts so as to provide their normal attendant functions. The additive package may include, but is not limited to, viscosity index improvers, corrosion inhibitors, oxidation inhibitors, coupling agents, dispersants, extreme pressure agents, color stabilizers, surfactants, diluents, detergents and rust inhibitors, pour point depressants, antifoaming agents, and antiwear agents.

The biodegradable two-cycle engine oil according to the present invention can employ typically about 75 to 85% base stock, about 1 to 5% solvent, with the remainder comprising an additive package.

Examples of the above additives for use in biodegradable lubricants are set forth in the following documents which are incorporated herein by reference: U.S. Patent No. 4,663,063 (Davis), which issued on May 5, 1987; U.S. Patent No. 5,330,667 (Tiffany, III et al.), which issued on July 19, 1994; U.S. Patent No. 4,740,321 (Davis et al.), which issued on April 26, 1988; U.S. Patent No. 5,321,172 (Alexander et al.), which issued on June 14, 1994; and U.S. Patent No. 5,049,291 (Miyaji et al.), which issued on September 17, 1991.

BIODEGRADABLE CATAPULT OILS

Catapults are instruments used on aircraft carriers at sea to eject the aircraft off of the carrier. The branched synthetic ester base stock can be used in the formulation of biodegradable catapult oils together with selected lubricant additives. The preferred biodegradable catapult oil is typically formulated using the biodegradable synthetic ester base stock formed according to the present invention together with any conventional catapult oil additive package. The additives listed below are typically used in such amounts so as to provide their normal attendant functions. The additive package may include, but is not limited to, viscosity index improvers, corrosion inhibitors, oxidation inhibitors, extreme

pressure agents, color stabilizers, detergents and rust inhibitors, antifoaming agents, antiwear agents, and friction modifiers.

5 The biodegradable catapult oil according to the present invention can employ typically about 90 to 99% base stock, with the remainder comprising an additive package.

10 Biodegradable catapult oils preferably include conventional corrosion inhibitors and rust inhibitors. If desired, the catapult oils may contain other conventional additives such as antifoam agents, antiwear agents, other antioxidants, extreme pressure agents, friction modifiers and other hydrolytic stabilizers. These additives are disclosed in Klamann, "Lubricants and Related Products", Verlag Chemie, Deerfield Beach, FL, 1984, which is incorporated herein by reference.

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BIODEGRADABLE HYDRAULIC FLUIDS

20 The branched synthetic ester base stock can be used in the formulation of biodegradable hydraulic fluids together with selected lubricant additives. The preferred biodegradable hydraulic fluids are typically formulated using the biodegradable synthetic ester base stock formed according to the present invention together with any conventional hydraulic fluid additive package. The additives listed below are typically used in such amounts so as to provide their normal attendant functions. The additive package may include, but is not limited to, viscosity index improvers, corrosion inhibitors, boundary lubrication agents, 25 demulsifiers, pour point depressants, and antifoaming agents.

30 The biodegradable hydraulic fluid according to the present invention can employ typically about 90 to 99% base stock, with the remainder comprising an additive package.

Other additives are disclosed in U.S. Patent No. 4,783,274 (Jokinen et al.), which issued on November 8, 1988, and which is incorporated herein by reference.

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BIODEGRADABLE DRILLING FLUIDS

The branched synthetic ester base stock can be used in the formulation of biodegradable drilling fluids together with selected lubricant additives. The preferred biodegradable drilling fluids are typically formulated using the
5 biodegradable synthetic ester base stock formed according to the present invention together with any conventional drilling fluid additive package. The additives listed below are typically used in such amounts so as to provide their normal attendant functions. The additive package may include, but is not limited to, viscosity index improvers, corrosion inhibitors, wetting agents, water loss improving agents,
10 bactericides, and drill bit lubricants.

The biodegradable drilling fluid according to the present invention can employ typically about 60 to 90% base stock and about 5 to 25% solvent, with the remainder comprising an additive package. See U.S. Patent No. 4,382,002
15 (Walker et al), which issued on May 3, 1983, and which is incorporated herein by reference.

Suitable hydrocarbon solvents include: mineral oils, particularly those paraffin base oils of good oxidation stability with a boiling range of from 200-
20 400°C such as Mentor 28®, sold by Exxon Chemical Americas, Houston, Texas; diesel and gas oils; and heavy aromatic naphtha.

BIODEGRADABLE WATER TURBINE OILS

The branched synthetic ester base stock can be used in the formulation of
25 biodegradable water turbine oils together with selected lubricant additives. The preferred biodegradable water turbine oil is typically formulated using the biodegradable synthetic ester base stock formed according to the present invention together with any conventional water turbine oil additive package. The additives listed below are typically used in such amounts so as to provide their normal
30 attendant functions. The additive package may include, but is not limited to, viscosity index improvers, corrosion inhibitors, oxidation inhibitors, thickeners, dispersants, anti-emulsifying agents, color stabilizers, detergents and rust inhibitors, and pour point depressants.

The biodegradable water turbine oil according to the present invention can employ typically about 65 to 75% base stock and about 5 to 30% solvent, with the remainder comprising an additive package, typically in the range between about 0.01 to about 5.0 weight percent each, based on the total weight of the composition.

BIODEGRADABLE GREASES

The branched synthetic ester base stock can be used in the formulation of biodegradable greases together with selected lubricant additives. The main ingredient found in greases is the thickening agent or gellant and differences in grease formulations have often involved this ingredient. Besides, the thickener or gellants, other properties and characteristics of greases can be influenced by the particular lubricating base stock and the various additives that can be used.

The preferred biodegradable greases are typically formulated using the biodegradable synthetic ester base stock formed according to the present invention together with any conventional grease additive package. The additives listed below are typically used in such amounts so as to provide their normal attendant functions. The additive package may include, but is not limited to, viscosity index improvers, oxidation inhibitors, extreme pressure agents, detergents and rust inhibitors, pour point depressants, metal deactivators, antiwear agents, and thickeners or gellants.

The biodegradable grease according to the present invention can employ typically about 80 to 95% base stock and about 5 to 20% thickening agent or gellant, with the remainder comprising an additive package.

Typically thickening agents used in grease formulations include the alkali metal soaps, clays, polymers, asbestos, carbon black, silica gels, polyureas and aluminum complexes. Soap thickened greases are the most popular with lithium and calcium soaps being most common. Simple soap greases are formed from the alkali metal salts of long chain fatty acids with lithium 12-hydroxystearate, the predominant one formed from 12-hydroxystearic acid, lithium hydroxide monohydrate and mineral oil. Complex soap greases are also in common use and comprise metal salts of a mixture of organic acids. One typical complex soap

grease found in use today is a complex lithium soap grease prepared from 12-hydroxystearic acid, lithium hydroxide monohydrate, azelaic acid and mineral oil. The lithium soaps are described and exemplified in many patents including U.S. Patent No. 3,758,407 (Harting), which issued on September 11, 1973; U.S. Patent
5 No. 3,791,973 (Gilani), which issued on February 12, 1974; and U.S. Patent No. 3,929,651 (Murray), which issued on December 30, 1975, all of which are incorporated herein by reference together with U.S. Patent No. 4,392,967 (Alexander), which issued on July 12, 1983.

10 A description of the additives used in greases may be found in Boner, "Modern Lubricating Greases", 1976, Chapter 5, which is incorporated herein by reference, as well as additives listed above in the other biodegradable products.

BIODEGRADABLE COMPRESSOR OILS

15 The branched synthetic ester base stock can be used in the formulation of biodegradable compressor oils together with selected lubricant additives. The preferred biodegradable compressor oil is typically formulated using the biodegradable synthetic ester base stock formed according to the present invention together with any conventional compressor oil additive package. The additives
20 listed below are typically used in such amounts so as to provide their normal attendant functions. The additive package may include, but is not limited to, oxidation inhibitors, additive solubilizers, rust inhibitors/metal passivators, demulsifying agents, and antiwear agents.

25 The biodegradable compressor oil according to the present invention can employ typically about 80 to 99% base stock and about 1 to 15% solvent, with the remainder comprising an additive package.

The additives for compressor oils are also set forth in U.S. Patent No.
30 5,156,759 (Culpon, Jr.), which issued on October 20, 1992, and which is incorporated herein by reference.

EXAMPLE 1

The following are conventional ester base stocks which do not exhibit
35 satisfactory properties for use as biodegradable lubricants. The properties listed in

Tables 1 and 2 were determined as follows. Pour Point was determined using ASTM # D-97. Brookfield Viscosity at -25°C was determined using ASTM # D-2983. Kinematic viscosity (@ 40 and 100°C) was determined using ASTM # D-445. Viscosity index (VI) was determined using ASTM # D-2270.

- 5 Biodegradation was determined using the Modified Sturm test (OECD Test No. 301B). Solubility with dispersant was determined by blending the desired ratios and looking for haze, cloudiness, two-phases, etc. Engine wear was determined using the NMMA Yamaha CE50S Lubricity test. Oxidation induction time was determined using a high pressure differential scanning calorimeter (HPDSC) having isothermal/isobaric conditions of 220°C and 500 psi (3.445 MPa) air, respectively. Aquatic toxicity was determined using the Dispersion Aquatic Toxicity test. The acid number was determined using ASTM # D-664. The hydroxyl number of the respective samples was determined by infrared spectroscopy.

15

Table 1

	Pour Point °C	Vis @ -25°C (cPs)	Vis. @ 40°C (cSt)	Vis. @ 100°C (cSt)	*Sol with % Bio. Disp.	Engine Wear
Base stock						
20 <u>Natural Oils</u>						
Rapeseed Oil	0	Solid	47.80	10.19	86.7 n/a	n/a
<u>All Linear Esters</u>						
Di-undecyladipate	+21	solid	13.92	2.80	n/a n/a	n/a
<u>Polyol w/Linear & Semi-Linear Acids</u>						
25 TPE/C810/C7 acid	n/a	solid	29.98	5.90	n/a n/a	n/a
TPE/DiPE/n-C7	-45	1380	24.70	5.12	82.31 H	Fail
TPE/C7 acid	-62	915	24.0	4.9	83.7 H	Fail
TMP/n-C7,8,10	-85	350	17.27	4.05	61.7** C	Fail
TMP/C7 acid	-71	378	14.1	3.4	76.5 C	Fail
30 <u>Branched Adipates</u>						
di-tridecyladipate	-62	n/a	26.93	5.33	65.99 C	Fail
<u>All Branched</u>						
TPE/Iso-C8 acid	-46	n/a	61.60	8.2	13.33 C	n/a

* denotes solubility with dispersant: H= haze; C= clear.

- 35 ** denotes the biodegradation for this material includes 15.5 wt% dispersant.

n/a denotes information was not available.

TPE denotes technical grade pentaerythritol.

TMP denotes trimethylolpropane.

C810 denotes predominantly a mixture of n-octanoic and n-decanoic acids, and

5 may include small amounts of n-C₆ and n-C₁₂ acids. A typical sample of C810 acid may contain, e.g., 3-5% n-C₆, 48-58% n-C₈, 36-42% n-C₁₀, and 0.5-1% n-C₁₂.

n-C_{7,8,10} denotes a blend of linear acids with 7, 8 and 10 carbon atoms, e.g., 37% mole % n-C₇ acid, 39 mole % C₈ acid, 21 mole % C₁₀ acid and 3 mole %
10 C₆ acid.

C7 denotes a C₇ acid produced by cobalt catalyzed oxo reaction of hexene-1, that is 70% linear and 30% α -branched. The composition includes approximately 70% n-heptanoic acid, 22% 2-methylhexanoic acid, 6.5% 2-ethylpentanoic acid, 1% 4-methylhexanoic acid, and 0.5% 3,3-dimethylpentanoic acid.
15

The properties of the branched ester base stock according to the present invention were compared against various conventional biodegradable lubricant base stocks and the results are set forth below in Table 2.

20

Table 2

Property	TPE/Ck8/C810	Rapeseed Oil	DTDA	TMP/iC18
Pour Point (°C)	-45	0	-54	-20
Flash Point (°C)	274	162	221	n/a
25 -25°C Viscosity (cps)	3600	solid	n/a	358,000
40°C Viscosity (cSt)	38.78	47.80	26.93	78.34
100°C Viscosity (cSt)	6.68	10.19	5.33	11.94
Viscosity Index	128	208	135	147
Oxidation Induction Time*	15.96	2.12	3.88	4.29
30 Lubricity (Yamaha Engine)	Pass	n/a	Fail	Pass
% Biodegradation (Mod. Sturm)	~85%	~85%	~60%	~65%
Toxicity (LC50, ppm)	>5000	>5000	<1000	n/a
Solubility with Dispersant	soluble	n/a	soluble	n/a
Acid Number (mgKOH/g)	0.01	0.35	0.04	1.9
35 Hydroxyl Number (mgKOH/g)	1.91	n/a	1.49	n/a

* Oxidation Induction Time is the amount of time (in minutes) for a molecule to oxidatively decompose under a particular set of conditions using a high pressure differential scanning calorimeter (HPDSC). The longer it takes (the greater the number of minutes), the more stable the molecule. This shows that the molecule of the present invention is almost four times more oxidatively stable than any of the materials currently in use. The conditions used to evaluate these molecules were: 220°C and 500 psi (3.447 MPa) air.

~ denotes approximately.

> denotes greater than.

10 < denotes less than.

DTDA denotes di-tridecyladipate.

TMP/iC18 denotes tri-ester of trimethylol propane and isostearic acid.

TPE denotes technical grade pentaerythritol.

TMP denotes trimethylolpropane.

15 C810 denotes a mixture of 3-5% n-C6, 48-58% n-C8, 36-42% n-C10, and 0.5-1.0% n-C12 acids.

Ck8 denotes Cekanioic-8 acid comprising a mixture of 26 wt.% 3,5-dimethyl hexanoic acid, 19 wt.% 4,5-dimethyl hexanoic acid, 17% 3,4-dimethyl hexanoic acid, 11 wt.% 5-methyl heptanoic acid, 5 wt.% 4 methyl heptanoic acid, and 22 wt.% of mixed methyl-heptanoic acids and dimethyl hexanoic acids.

20

The data set forth in Table 2 above demonstrates that the TPE/C810/Ck8 biodegradable ester base stock according to the present invention is superior to rapeseed oil in cold flow properties and stability. The data also shows that the TPE/C810/Ck8 biodegradable ester base stock is superior to di-tridecyladipate in stability, biodegradation, and aquatic toxicity. The ester base stock according to the present invention is also superior to TMP/iso-C18 in cold flow properties, stability, and biodegradation.

Rapeseed oil, a natural product, is very biodegradable, but it has very poor low temperature properties and does not lubricate very well due to its instability. Rapeseed oil is very unstable and breaks down in the engine causing deposit formation, sludge and corrosion problems. The di-undecyladipate, while probably biodegradable, also has very poor low temperature properties. Polyol esters of low molecular weight linear acids do not provide lubricity, and those of high molecular weight linear or semi-linear acids have poor low temperature properties.

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In addition, the pentaerythritol esters of linear acids are not soluble with polyamide dispersants. The di-tridecyladipate is only marginally biodegradable and, when blended with a dispersant that has low biodegradability, the formulated oil is only about 45% biodegradable. In addition, the di-tridecyladipate does not provide
 5 lubricity. Lower molecular weight branched adipates such as di-isodecyladipate, while more biodegradable, also do not provide lubricity and can cause seal swell problems. Polyol esters of trimethylolpropane or pentaerythritol and branched oxo acids do not biodegrade easily due to the steric hindrance discussed earlier.

10

EXAMPLE 2

The present inventors have discovered that highly biodegradable base stocks with good cold flow properties, good solubility with dispersants, and good lubricity can be achieved by incorporating branched acids into the ester molecule. The data set forth in Table 3 below demonstrates that all of the desired base stock
 15 properties can be best met with polyol esters incorporating 20 to 70% of a highly branched oxo acid and 30 to 80% of a linear acid.

Table 3

Base stock	Pour Point °C	Vis @ -25°C (cPs)	Vis. @ 40°C (cSt)	Vis. @ 100°C (cSt)	% Bio	*Sol with Disp.	Engine Wear
TPE/C810/Ck8	-36**	7455**	34.87	6.37	99.54	C	Pass
TPE/C810/Ck8 and TMP/n-C7,8,10***	-56	610	24.90	5.10	81.0	C	Pass
25 TPE/C810/Ck8 and TPE/1770****	-46	910	30.48	5.75	85.5	H	Pass

* Denotes solubility with dispersant: H= haze; C= clear.

** Denotes Pour Point and -25°C Viscosity of Base stock with Dispersant.

*** Denotes a 50:50 weight % ratio of TPE/C810/Ck8 and TMP/7810.

30 **** Denotes a 50:50 weight % ratio of TPE/C810/Ck8 and TPE/1770.

1770 denotes a 70:30 mix of n-C₇ acid (70%) and alpha-branched C₇ acids (30%). The composition includes approximately 70% n-heptanoic acid, 22% 2-methylhexanoic acid, 6.5% 2-ethylpentanoic acid, 1% 4-methylhexanoic acid, and 0.5% 3,3-dimethylpentanoic acid.

35 TPE denotes technical grade pentaerythritol.

TMP denotes trimethylolpropane.

C810 denotes a mixture of 3-5% n-C6, 48-58% n-C8, 36-42% n-C10, and 0.5-1.0% n-C12 acids.

Ck8 denotes Cekanoic-8 acid comprising a mixture of 26 wt.% 3,5-dimethyl hexanoic acid, 19 wt.% 4,5-dimethyl hexanoic acid, 17% 3,4-dimethyl hexanoic acid, 11wt.% 5-methyl heptanoic acid, 5 wt.% 4 methyl heptanoic acid, and 22 wt.% of mixed methyl heptanoic acids and dimethyl hexanoic acids.

n-C7,8,10 denotes a blend of linear acids with 7, 8 and 10 carbon atoms, e.g., 37% mole % n-C₇ acid, 39 mole % C₈ acid, 21 mole % C₁₀ acid and 3 mole % C₆ acid.

The data in Table 3 above shows that the polyol ester of technical grade pentaerythritol, iso-C8 and linear C810 acids can be used alone or in combination with other lower molecular weight esters as a biodegradable lubricant. These esters are particularly useful when lower viscosities are needed for a variety of biodegradable lubricant applications. The TPE/C810/Ck8 ester provides sufficient lubricity such that, even when diluted with other materials, it can meet the lubricity requirements without the addition of wear additives. When additives such as polyisobutylene, EP (extreme pressure) wear additives, corrosion inhibitors, or antioxidants are needed, the biodegradability of the final product can be reduced and the toxicity increased. If the base stock provides the needed properties without additives or if the additives needed can be minimized, the final product reflects the biodegradability and toxicity of the base stock, which in this case are high and low, respectively.

EXAMPLE 3

A sample of an ester base stock was prepared in accordance with the present invention wherein 220 lbs. (99.8 kg) of a C810 acid and 205 lbs. (93 kg) of Cekanoic 8 acid (a 50:50 molar ratio) were loaded into a reactor vessel and heated to 430°F (221°C) at atmospheric pressure. Thereafter, 75 lbs. (34 kg) of technical grade pentaerythritol were added to the acid mixture and the pressure was dropped until water began evolving. The water was taken overhead to drive the reaction. After about 6 hours of reaction time, the excess acids were removed overhead until a total acid number of 0.26 mgKOH/g was reached for the reaction product. The product was then neutralized and decolored for two hours at 90°C with twice the stoichiometric amount of Na₂CO₃ (based on acid number) and 0.15 wt.% admix

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(based on amount in the reactor). The admix is a blend of 80 wt.% carbon black and 20 wt.% dicalite. After two hours at 90°C, the product was vacuum filtered to remove solids.

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The properties set forth below in Table 4 were measured on the product:

Table 4

10	Total Acid Number	0.071 mgKOH/g
	Specific Gravity	0.9679
	Pour Point	-45°C
	ppm Water	97
	Flash Point (COC)	285°C
15	Oxidation Induction Time (min.)	15.96
	Viscosity @ -25°C	3950 cps
	Viscosity @ 40°C	38.88 cSt
	Viscosity @ 100°C	6.66 cSt
	Viscosity Index	127

20

An acid assay (saponification) was performed on the product in order to ascertain the amount of each acid actually on the molecule. Table 5 below sets forth the molar amounts of each acid on the product ester:

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Table 5

Cekanoic 8 Acid	43.35%
n-C ₈ Acid	35.73%
nC ₁₀ Acid	20.92%

30

This resultant ester product was then submitted with and without additives for biodegradation tests for application into the hydraulic fluid market. The additives were used at a 2-5 wt.% treat rate. The results are set forth below in Table 6.

35

Table 6

Product	% Biodeg.	Standard Deviation	Meet 10 day Window
TPE/C810/Ck8 (alone)	92.9	± 7.0	yes
5 TPE/C810/Ck8 + BIO SHP Adpack*	80.5	± 1.6	no
TPE/C810/Ck8 + MGG Adpack***	75.4	± 6.9	no
TPE/C810/Ck8 + Synestic Adpack**	76.8	±14.7	no

* Denotes a lubricant additive package sold by Exxon Company, USA, under the trademark Univis BIO SHP Adpack.

10 ** Denotes a lubricant additive package sold by Exxon Chemical Company, Paramins Division under the trademark Synestic Adpack.

*** Denotes a lubricant additive package sold by Exxon Company, USA under the trademark MGG Adpack.

15 The resultant ester base stock formed in accordance with this Example 3 was also blended at a 50:50 wt.% ratio with the ester TMP/7810. This blend was submitted with and without additives for biodegradation tests for application into the two-cycle engine oil market. The additives were used at a 14-16 wt.% treat rate. The results are set forth in Table 7 below.

20

Table 7

Product	% Biodeg.	Standard Deviation
TPE/C810/Ck8 + TMP/7810 (50:50)	80.7	±3.6
25 TPE/C810/Ck8 + TMP/7810 + 14.5 wt.% Dispersant*	76.1	±4.6

* The dispersant package comprising primarily of polyamides.

EXAMPLE 4

30 Table 8 below contains comparative data for all-linear and semi-linear esters verses the biodegradable synthetic ester base stock formed according to the present invention. We have provided two examples of the ester base stock according to the present invention because they contain two different molar ratios of Cekanoic 8 to C810. The results indicate that a certain amount of branching does not greatly affect biodegradation as measured by the Modified Sturm test and
35 may, in fact, actually improve it which is contrary to conventional wisdom.

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Table 8

	Ester	% Biodegradation (28 Days)	Standard Deviation	10-Day Window
	Totally Linear Ester			
5	TMP/7810	76.13	8.77	no
	TPE/Di-PE/n-C ₇	82.31	6.25	yes
	L9 Adipate	89.63	6.28	yes
	MPD/AA/C810	86.09	3.76	yes
	Semi-Linear Ester			
10	TMP/isostearate	63.32	1.91	no
	TMP/1770	76.46	1.58	no
	TMP/1770	83.65	6.89	no
	Branched Ester			
	TPE/C810/Ck8*	92.90	7.00	yes
15	TPE/C810/Ck8**	99.54	1.85	yes

Notes: TMP/7810 denotes a tri-ester of trimethylpropane and C₇, C₈ and C₁₀ acids.

TPE/Di-PE/n-C₇ denotes esters of technical grade pentaerythritol, di-pentaerythritol and n-C₇ acid.

20 L9 Adipate denotes a di-ester of adipic acid and n-C₉ alcohol.

MPD/AA/C810 denotes a complex ester of 2-methyl-1,3-propanediol (2 mols), adipic acid (1 mol) and n-C₈ and C₁₀ acids (2 mol).

Rapeseed Oil is a tri-ester of glycerol and stearic acid.

25 TMP/isostearate denotes a tri-ester of trimethylpropane and iso-stearic acid (1 methyl branch per acid chain).

30 TMP/1770 denotes a tri-ester of trimethylpropane and a 70:30 mix of n-C₇ acid (70%) and alpha-branched C₇ acids (30%). The 1770 composition includes approximately 70% n-heptanoic acid, 22% 2-methylhexanoic acid, 6.5% 2-ethylpentanoic acid, 1% 4-methylhexanoic acid, and 0.5% 3,3-dimethylpentanoic acid.

35 TPE/1770 denotes esters of technical grade pentaerythritol and a 70:30 mix of n-C₇ acid (70%) and alpha-branched C₇ acids (30%). The 1770 composition includes approximately 70% n-heptanoic acid, 22% 2-methylhexanoic acid, 6.5% 2-ethylpentanoic acid, 1% 4-methylhexanoic acid, and 0.5% 3,3-dimethylpentanoic acid.

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* TPE/C810/Ck8 denotes esters of technical grade pentaerythritol and a 45:55 molar ratio of iso-C₈ acid (Ck8) and C810 acid.

** TPE/C810/Ck8 denotes esters of technical grade pentaerythritol and a 30:70 molar ratio of iso-C₈ acid (Ck8) and C810 acid.

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WHAT IS CLAIMED IS

1. A biodegradable synthetic ester base stock which comprises the reaction product of:

a branched or linear alcohol having the general formula $R(OH)_n$,

5 wherein R is an aliphatic or cyclo-aliphatic group having from about 2 to 20 carbon atoms and n is at least 2; and

mixed acids comprising about 30 to 80 molar % of a linear acid having a carbon number in the range between about C_5 to C_{12} , and about 20 to 70 molar % of at least one branched acid having a carbon number in the range
10 between about C_5 to C_{13} ; wherein said ester base stock exhibits the following properties: at least 60% biodegradation in 28 days as measured by the Modified Sturm test; a pour point of less than -25°C ; and a viscosity of less than 7500 cps at -25°C .

15 2. The biodegradable synthetic ester base stock according to claim 1 wherein said linear acid has a carbon number in the range between about C_7 to C_{10} .

3. The biodegradable synthetic ester base stock according to claim 1 wherein said mixed acids comprise said linear acid in an amount of about 35 to 55
20 molar %.

4. The biodegradable synthetic ester base stock according to claim 1 wherein said branched acid has a carbon number in the range between about C_7 to C_{10} .
25

5. The biodegradable synthetic ester base stock according to claim 3 wherein said mixed acids comprise said branched acid in an amount of about 35 to 55 molar %.

30 6. The biodegradable synthetic ester base stock according to claim 1 wherein said branched acid comprises multiple isomers.

7. The biodegradable synthetic ester base stock according to claim 6 wherein said branched acid comprises at least 3 isomers.

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8. The biodegradable synthetic ester base stock according to claim 7 wherein said branched acid has between about greater than 3 to 5 isomers.

9. The biodegradable synthetic ester base stock according to claim 1
5 wherein said linear acid is selected from the group of alkyl mono-carboxylic acids or di-carboxylic acids.

10. The biodegradable synthetic ester base stock according to claim 1 wherein said linear acid has the general structure RCOOH , wherein R is a linear
10 alkyl group having from about 4 to 11 carbon atoms.

11. The biodegradable synthetic ester base stock according to claim 1 wherein said ester also exhibits a high flash point COC of at least 175°C .

12. The biodegradable synthetic ester base stock to claim 1 wherein
15 said branched or linear alcohol is selected from the group consisting of: technical grade pentaerythritol, mono-pentaerythritol, di-pentaerythritol, neopentylglycol, trimethylolpropane, ethylene or propylene glycol, butane diol, sorbitol, and 2-methylpropane diol.

20

13. The biodegradable synthetic ester base stock according to claim 1 wherein said branched acid is predominantly a doubly branched or an alpha branched acid having an average branching per molecule in the range between about 0.3 to 1.9.

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14. The biodegradable synthetic ester base stock according to claim 4 wherein said branched acid is at least one acid selected from the group consisting of: 2-ethylhexanoic acids, isoheptanoic acids, isooctanoic acids, isononanoic acids, and isodecanoic acids.

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15. The biodegradable synthetic ester base stock according to claim 1 wherein no more than 10% of said branched acids used to form said biodegradable synthetic ester base stock contain a quaternary carbon.

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16. A biodegradable lubricant which is prepared from
at least one biodegradable synthetic ester base stock which
comprises the reaction product of: a branched or linear alcohol having the general
formula $R(OH)_n$, wherein R is an aliphatic or cyclo-aliphatic group having from
5 about 2 to 20 carbon atoms and n is at least 2; and mixed acids comprising about
30 to 80 molar % of a linear acid having a carbon number in the range between
about C_5 to C_{12} , and about 20 to 70 molar % of at least one branched acid having a
carbon number in the range between about C_5 to C_{13} ; wherein said ester base stock
exhibits the following properties: at least 60% biodegradation in 28 days as
10 measured by the Modified Sturm test; a pour point of less than -25°C ; and a
viscosity of less than 7500 cps at -25°C ; and
a lubricant additive package.
17. The biodegradable lubricant according to claim 16 wherein said
15 linear acid has a carbon number in the range between about C_7 to C_{10} .
18. The biodegradable lubricant according to claim 16 wherein said
mixed acids comprise said linear acid in an amount of about 35 to 55 molar %.
- 20 19. The biodegradable lubricant according to claim 16 wherein said
branched acid has a carbon number in the range between about C_7 to C_{10} .
20. The biodegradable lubricant according to claim 18 wherein said
mixed acids comprise said branched acid in an amount of about 35 to 55 molar %.
- 25 21. The biodegradable lubricant according to claim 16 wherein said
branched acid comprises multiple isomers.
22. The biodegradable lubricant according to claim 21 wherein said
30 branched acid comprises at least 3 isomers.
23. The biodegradable lubricant according to claim 22 wherein said
branched acid comprises between about greater than 3 to 5 isomers.





24. The biodegradable lubricant according to claim 16 wherein said linear acid is selected from the group of alkyl mono-carboxylic acids or di-carboxylic acids.

5 25. The biodegradable lubricant according to claim 16 wherein said linear acid has the general structure RCOOH , wherein R is a linear alkyl group having from about 4 to 11 carbon atoms.

26. The biodegradable lubricant according to claim 16 wherein said
10 ester base stock also exhibits a high flash point COC of at least 175°C .

27. The biodegradable lubricant according to claim 16 wherein said branched or linear alcohol is selected from the group consisting of: technical grade pentaerythritol, mono-pentaerythritol, di-pentaerythritol, neopentylglycol,
15 trimethylolpropane, ethylene or propylene glycol, butane diol, sorbitol, and 2-methylpropane diol.

28. The biodegradable lubricant according to claim 16 wherein said branched acid is predominantly a doubly branched or an alpha branched acid
20 having an average branching per molecule in the range between about 0.3 to 1.9.

29. The biodegradable lubricant according to claim 19 wherein said branched acid is at least one acid selected from the group consisting of: 2-ethylhexanoic acids, isoheptanoic acids, isooctanoic acids, isononanoic acids, and
25 isodecanoic acids.

30. The biodegradable lubricant according to claim 16 wherein said biodegradable lubricant is a blend of said branched synthetic esters.

30 31. The biodegradable lubricant according to claim 16 wherein said additive package comprises additives selected from the group consisting of: viscosity index improvers, corrosion inhibitors, oxidation inhibitors, dispersants, lube oil flow improvers, detergents and rust inhibitors, pour point depressants, anti-foaming agents, antiwear agents, seal swellants, and friction modifiers.





32. The biodegradable lubricant according to claim 16 wherein said biodegradable lubricant is a catapuit oil.

5 33. The biodegradable lubricant according to claim 32 wherein said additive package comprises at least one additive selected from the group consisting of: viscosity index improvers, corrosion inhibitors, oxidation inhibitors, coupling agents, dispersants, extreme pressure agents, color stabilizers, detergents and rust inhibitors, antifoaming agents, antiwear agents, and friction modifiers.

10 34. The biodegradable lubricant according to claim 16 wherein said biodegradable lubricant is a hydraulic fluid.

15 35. The biodegradable lubricant according to claim 34 wherein said additive package comprises at least one additive selected from the group consisting of: viscosity index improvers, corrosion inhibitors, boundary lubrication agents, demulsifiers, pour point depressants, and antifoaming agents.

20 36. The biodegradable lubricant according to claim 16 wherein said biodegradable lubricant is a drilling fluid.

25 37. The biodegradable lubricant according to claim 36 wherein said additive package comprises at least one additive selected from the group consisting of: viscosity index improvers, corrosion inhibitors, weighting agents, water loss improving agents, bactericides, and drill bit lubricants.

38. The biodegradable lubricant according to claim 16 wherein said biodegradable lubricant is a water turbine oil.

30 39. The biodegradable lubricant according to claim 38 wherein said additive package comprises at least one additive selected from the group consisting of: viscosity index improvers, corrosion inhibitors, oxidation inhibitors, thickeners, dispersants, anti-emulsifying agents, color stabilizers, detergents and rust inhibitors, and pour point depressants.





40. The biodegradable lubricant according to claim 16 wherein said biodegradable lubricant is a grease.

41. The biodegradable lubricant according to claim 40 wherein said
5 additive package comprises at least one additive selected from the group consisting of: thickening agent, viscosity index improvers, oxidation inhibitors, extreme pressure agents, detergents and rust inhibitors, pour point depressants, metal deactivators, and antiwear agents.

10 42. The biodegradable lubricant according to claim 16 wherein said biodegradable lubricant is a compressor oil.

43. The biodegradable lubricant according to claim 42 wherein said
15 additive package comprises at least one additive selected from the group consisting of: oxidation inhibitors, detergents and rust inhibitors, metal deactivators, additive solubilizers, demulsifying agents, and antiwear agents.

44. The biodegradable lubricant according to claim 16 wherein no more
20 than 10% of said branched acids used to form said biodegradable synthetic ester base stock contain a quaternary carbon.

45. The biodegradable lubricant according to claim 16 further comprising a solvent.

25 46. The biodegradable lubricant according to claim 45 wherein said biodegradable synthetic ester base stock is present in an amount of about 50-99 % by weight, said lubricant additive package is present in an amount of about 1 to 20 % by weight lubricant additive package; and solvent is present in an amount of about 0 to 30 %.

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47. The biodegradable lubricant according to claim 16 wherein said biodegradable lubricant is a two-cycle engine oil.

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48. The biodegradable lubricant according to claim 47 wherein said additive package includes at least one additive selected from the group consisting of: viscosity index improvers, corrosion inhibitors, oxidation inhibitors, coupling agents, dispersants, extreme pressure agents, color stabilizers, surfactants, diluents, 5 detergents and rust inhibitors, pour point depressants, antifoaming agents, and antiwear agents.

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This Sheet Has Been Replaced

