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POLYMERIC LUBRICANT COMPOSITIONS, AND METHODS FOR THEIR USE

FIELD OF THE INVENTION

This invention relates to the lubricant field and especially to textile lubricants.

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BACKGROUND OF THE INVENTION

There are two fundamental classes of lubricating agents - natural and synthetic. Lubricating oils are fluids whose function is the reduction of friction and wear between solid surfaces in relative motion.

While the major portion of industrial lubricants is derived from petroleum, synthetic lubricants are becoming of increasing importance. Synthetic lubricants include the following:

- (1) Natural liquid fatty esters, such as lard oil, palm oil, sperm oil, etc. These are good lubricants but have poor chemical stability.
- (2) Synthetic hydrocarbons, prepared by polymerization of olefinic hydrocarbons; these have good stability when saturated and good viscosity-temperature coefficients.
- (3) Polyalkylene glycol oils, made by reaction of alcohols with polymerized ethylene and propylene glycols. They are either water-soluble or -insoluble. They have air stability (improved with additives), good viscosity temperature coefficient, and good lubricating qualities.
- (4) Synthetic esters, including (a) esters of dibasic acids such as adipic and sebacic, and esters based on monobasic acids, (b) organic esters of phosphoric and silicic acid, which have some advantage of being more fire-resistant than the other organic compounds but which are subject to hydrolysis on exposure to water.
- (5) Silicone oils, which are linear and cyclic siloxane polymers of the formula $(-SiR_2O)_n$. They generally possess good thermal and oxidative stability, and good viscosity-temperature coefficients. When -R is a

hydrocarbon substituent their lubricating ability is poor. This can be somewhat improved by the introduction of an aromatic halogen in -R.

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(6) Halogenated hydrocarbons (chlorinated or fluorinated). These have good lubricating properties but very poor viscosity-temperature relations. The fluorinated materials are extremely stable.

- (7) Perfluorinated polyalkylene glycols which have better viscositytemperature behavior and temperature behavior and temperature resistance.
- (8) Polyphenyl ethers are very stable organic fluids which can be used in the 500-700°F (260-371°C) temperature range although, like the silicones, they do not have good boundary lubrication properties. These reportedly, however, can be improved with suitable additives.

There is a continuing need for synthetic lubricants that are thermally stable with good lubricating properties, and which in addition are biodegradable.

SUMMARY OF THE INVENTION

This invention relates to compositions containing polymeric material and to methods for their use as synthetic lubricants, having particular importance as lubricants for the fiber spinning process.

The polymeric materials having utility in the methods of the invention as synthetic lubricating oils are the following:

- A. at least one compound which is the reaction product under basic conditions of the following reactants:
 - a) at least one member selected from the group consisting of R¹(O-A)_aOH and R¹(O-A)_aNH₂ (III);
 - b) at least one member selected from the group consisting of R⁶(OA"),OH and R⁶(OA"),NH₂ (V);
 - c) at least one member selected from the group consisting of $HO(A'O)_{n}H$ and $H_{2}N(A'-O)_{n}A'NH_{2}$ (IV);
 - d) at least one linking compound of the formula YR^2 - $(Y')_dY''$; and
- e) optionally a compound of the formula R⁵Y'" and R³Y"" wherein:

R¹ and R⁶ are monovalent hydrophobic groups having from 4 to about 50 carbon atoms, independently selected from the group consisting of an aliphatic group, an aromatic group, and an aralkyl group;

R² is selected from the group consisting of aliphatic, substituted aliphatic, aromatic, or substituted aromatic groups, each group being divalent or trivalent;

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R³ and R⁵ are independently selected from hydrogen, lower alkyl, lower aralkyl, or are larger organic groups as later described;

Y, Y', Y'', are independently selected from the group consisting of halo, epoxy and carboxyl, Y''' and Y'''' are selected from the group consisting of halo and hydroxyl;

each of a, b, c, d, and n are integers, wherein each of a and c is independently any integer from 0 to about 200, preferably from 2 to 50; b is any integer from 0 to about 450, preferably from 2 to about 200; d is zero or 1; and n is any integer from 0 to about 450, preferably 2 to about 200; and

each of A, A', and A" is independently an alkylene group containing from 2 to 36 carbon atoms, preferably an ethylene, 1,2-propylene, 1,2-butylene group or combinations thereof;

wherein component b) can be identical to or different from component a); and/or

B. at least one compound which is the product of the reaction between compounds comprising a linking agent of formula I

$$R(Y)_3 (I)$$

wherein each Y group is a halogen atom or one Y group is a halogen atom and two Y groups with two adjacent carbon atoms in the R group and an oxygen atom form an epoxy group, and R is an alkanetriyl group containing from 3 to 10 carbon atoms; and a compound having the formula (II)

$$R^{7}(EO)_{n}(PO)_{m}(BO)_{n}X$$
 (II)

wherein R⁷ is a substituted or unsubstituted, saturated or unsaturated, organic oxy or thio group having from 1 to 36 carbon atoms or a secondary amino group having from 2 to 36 carbon atoms; n is a number from 0 to 50, e.g., from 1 to 50; m is a number of from 0 to 50, e.g., from 1 to 50; p is a number

of from 0 to 50 e.g., from 1 to 50; and X is hydrogen, or X can be a mercapto group or an amino group in place of a terminal -OH group, provided that when X is mercapto or amino; the sum of n, m, and p must be at least 1. The above organic group is preferably a substituted or unsubstituted, saturated or unsaturated, aliphatic or araliphatic oxy or thio group.

In the product of the reaction between the linking agent of formula I and the compound of formula II, the mole ratio or I:II is from 0.2:1 to 5:1, preferably from 0.4:1 to 2:1, and more preferably from 0.6:1 to 1.4:1.

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The preferred component B. is at least one compound which is the reaction product of an epihalohydrin and a compound of the formula VII

R8(EO)₀(PO)_mOH (VII)

wherein R⁸ is a substituted or unsubstituted, saturated or unsaturated aliphatic oxy group having from 4 to 22 carbon atoms; n is a number from 0 to 50, preferably from 2 to 20, and m is a number from 0 to 50 preferably 2 to 20; wherein the mole ratio of epihalohydrin to (II) is from about 0.60/1 to about 5/1, preferably from about 0.80/1 to about 2/1.

The above reaction products or mixtures thereof can be used alone in the methods of the invention or can be mixed with polyester lubricating oils in a mole ratio of from 99:1 to 10:90.

DETAILED DESCRIPTION OF THE INVENTION

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

The method of the invention comprises reducing friction and wear between solid surfaces which are, or which are to be, in relative motion, comprising applying to at least one of the solid surfaces a lubricating oil of the invention.

The lubricating oils of the invention can be used to lubricate solid surfaces where elevated operating temperatures are present. They are accordingly useful in the lubrication of ball bearings, pumps, turbines, in military and civilian aircraft engines, as automotive hydraulic brake fluids, as

compressor lubricants, as rubber lubricants, and especially as textile lubricants in spinning finishes.

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Spinning finishes are used in the production and processing of synthetic fibers. These spinning finishes all contain so-called textile lubricants to reduce friction between filaments or fibers and between filaments and guide elements. Specialized technology has made greater demands on fiber-to-metal lubricants. In particular, high-speed knitting apparatus used to knit cotton yarn at yarn speeds of from about 800 to 1200 rpm or m/min has generated friction levels which are not satisfactorily reduced by standard wax-emulsion type lubricants. This problem is exacerbated when textile yarns are wet-processed, as is frequently the case, since processing friction levels increase as the yarn moisture level rises. This effect is particularly pronounced with wet cotton yarn.

The spinning finishes of the invention provide an improved lubricant for textile yarns to reduce fiber-to-metal friction during processing, and, in particular, provide a lubricant which imparts substantially uniform low yarn friction effects regardless of yarn moisture level.

The spinning finishes of the inventions are applied to the fibers in amounts sufficient to reduce friction coefficients to the desired level, without leaving undesirably high residues on the fibers. Generally, amounts of lubricant applied will broadly correspond to amounts of wax-emulsion type lubricants customarily employed for a particular fiber type and operating conditions.

The spinning finishes, which have a temperature of 18° to 60°C, are applied by means of applicator rolls or at metering points via suitable applicators. Spinning finishes in the form of aqueous dispersion with a total active substance content of around 3 to 40% by weight and, more particularly, between 5 and 30% by weight are preferred. Based on the total active substance content, the spinning finishes according to the invention contain

- a) 35 to 100% by weight of the textile lubricant according to the invention,
- b) 0 to 65% by weight of emulsifiers, antistatic agents, wetting

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agents, and/or additives such as antioxidants, e.g. butylated hydroxytoluene, dialkyl or diaryl phosphonates, trialkyl or triaryl phosphates, ascorbic or citric acid and derivatives thereof, and the sterically hindered phenols disclosed in U.S. 5,464,546, incorporated herein by reference, thermal stabilizing agents, e.g. esters of thiocarboxylic acids corresponding to general formula (1) and/or (2):

$$R^1-S-R^2-COOH$$
 (1)

$$HOOC-R^3-S-R^4-COOH$$
 (2)

in which R¹, R², R³ and R⁴ may be the same or different and represent an alkyl, cycloalkyl, aryl or alkaryl group containing 1 to 22 carbon atoms, which are generally used in quantities of from 0.05 to 8% by weight based on the weight of lubricant, as disclosed in U.S. 5,478,485, which is incorporated by reference, and the high molecular weight acrylamidoalkane sulfonic acid polymer additive disclosed in U.S. 4,919,828, also incorporated herein by reference,

c) 0 to 10% by weight of pH regulators, and/or bactericides, the quantities being selected so that they add up to 100% by weight.

With respect to the reaction product of component A, it is believed that the reaction product is comprised of at least one compound of formula VI: $R^{1}-(O-A)_{a}-B^{1}-R^{2}-(B^{2}-R^{3})_{d}-(B^{3}-(A'-O)_{b-f}-(A'-B^{4})_{f}-R^{4}-(B^{5}-R^{5})_{e})_{n}-B^{6}-(A"O)_{c}-R^{6} \qquad (VI)$ wherein:

R¹ and R⁶ are monovalent hydrophobic groups independently selected from the group consisting of an aliphatic group, a substituted aliphatic group, an aromatic group, and a substituted aromatic group;

R² and R⁴ are independently selected from the group consisting of aliphatic, substituted aliphatic, aromatic, or substituted aromatic groups, each group being divalent or trivalent, and wherein R² and R⁴ are preferably independently selected from the group consisting of alkanetriyl groups having from 2 to 10 carbon atoms and aralkylene groups having one benzenoid ring

and from 1 to 10 aliphatic carbon atoms;

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R³ and R⁵ are independently selected from hydrogen, lower alkyl and lower aralkyl or are larger organic groups as later described,

B¹, B², B³, B⁴, B⁵, and B⁶ are linking groups independently selected from the group consisting of an oxygen atom (to form the ether linkage -O-), a carboxylate group (to form an ester linkage R²-C(O)-O- and/or R⁴-C(O)-O-), an amino group (to form the amine linkage R²-N(R)- and/or R⁴-N(R)-, wherein R is hydrogen, lower alkyl, lower aralkyl, or lower acyl), and an amido group (to form the amide linkage R²-N(R)-C(O)- and/or R⁴-N(R)-C(O)-, wherein R is hydrogen, lower alkyl, lower aralkyl, or lower acyl);

each of a, b, c, d, e, f, and n are integers, wherein each of a and c is independently any integer from 0 to about 200 preferably from 2 to 50; b is any integer from 0 to about 450, preferably from 2 to about 200; d, e, and f are zero or 1; and n is any integer from 0 to about 450, preferably 2 to about 200; and

each of A, A', and A" is independently an alkylene group containing from 2 to 36 carbon atoms, preferably ethylene, 1,2-propylene, 1,2-butylene group or combinations thereof.

In preferred compounds of formula VI, each of R¹ and R⁶ is independently an aliphatic, substituted aliphatic, aromatic, or substituted aromatic radical having from 4 to about 50 carbon atoms; each of B¹ - B⁶ is an oxygen atom; R² and R⁴ are both either propanetriyl groups having from 2 to 10 carbon atoms or meta-xylyl; d and e are either (i) both zero (e.g. when R² and R⁴ are both meta-xylyl) or (ii) both 1, and R³ and R⁵ are hydrogen, methyl or benzyl (e.g. when R² and R⁴ are both propanetriyl); f is zero; each of A, A′, and A″ are ethylene, n is 1, b is from 2 to about 200, and the values of a and c independently range from about 2 to about 50.

With respect to formula VI, the abbreviations A, A', and A" preferably stand for the ethylene group (-CH₂CH₂-), the 1,2-propylene group -(CH₂CH(CH₃)-), or the 1,2-butylene group (-CH(CH₂CH₃)CH₂-) or combinations thereof. Each of the subscripts a, b, c, f, and n are independently any integer as set forth above. One of ordinary skill in the art

will appreciate that for mixtures of pure compounds, the subscripts a, b, c, f, and n will have non-integer values to reflect the fact that they represent the average degree of polymerization.

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R² and R⁴ are aliphatic, substituted aliphatic, aromatic, or substituted aromatic groups having a valence of from 2 or 3. Such aliphatic groups include any di- or trivalent group: (a) straight chain and branched alkyl groups having from 2 to about 50 carbon atoms (preferably divalent or trivalent alkylene groups having from 2 to 10 carbon atoms); (b) cycloalkyl groups having from 4 to about 20 carbon atoms; (c) straight chain and branched alkenyl groups having from 2 to about 40 carbon atoms; (d) cycloalkenyl groups having from 5 to about 20 carbon atoms; (e) straight chain and branched alkynyl groups having from 2 to about 30 carbon atoms; cycloalkynyl groups having from 6 to about 20 carbon atoms; and (f) aralkyl groups (i.e. alkyl groups having aromatic groups as pendent substituents or linking alkylene groups) having at least 2 aliphatic carbon atoms along with an aromatic group, e.g. meta-xylyl wherein methylene groups are linked by a benzenoid group). Aliphatic groups also include those above mentioned aliphatic groups which contain one or more heteroatoms substituted for one or more hydrogen atoms. The heteroatoms include the halogens, nitrogen, sulfur, oxygen, and phosphorus or groups of heteroatoms such as nitro, sulfonic acid, C₁₋₁₀ alkyl sulfonate ester, sulfoxide, sulfone, phosphoryl, trihalomethyl, and the like. For purposes of this invention, it is understood that aliphatic includes cycloaliphatic and heterocycloaliphatic wherein the heteroatoms are nitrogen, oxygen, sulfur, and phosphorus.

The R² and R⁴ groups can be the same or are different when more than one linking compound (component Ad)) is employed. R² and R⁴ are of course identical when only one linking compound is used.

An aromatic radical is any benzenoid or non-benzenoid aromatic radical having a valence of 2 to 8. A non-benzenoid aromatic radical includes carbocyclic and heterocyclic aromatic radicals. For purposes of this invention, a substituted aromatic radical is any benzenoid or non-benzenoid aromatic radical having a valence of from 2 to 6 wherein one or more

hydrogen atoms is replaced by an atom or a group of atoms other than hydrogen including the halogens, nitrogen, sulfur, oxygen, and phosphorus or groups of heteroatoms such as nitro, sulfonic acid, C_{1-10} alkyl sulfonate ester, sulfoxide, sulfone, phosphoryl, trihalomethyl, and the like.

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The abbreviations NP, DNP, LA, and TD stand for nonylphenoxy. dinonylphenoxy, lauryl, and tridecyl, respectively. R¹ and R⁶ are monovalent groups, typically having from about 6 to about 50 carbon atoms. The use of a hydrophobic alcohol to form the ends of the compound of formula VI described above results in the formation of hydrophobic ether residues as R1 and R⁶. A hydrophobic group is any group which contributes to the water insolubility of the ether residue. Unsubstituted aliphatic groups having at least 6 carbon atoms, aromatic groups having 6 or more carbon atoms and groups which contain both aliphatic and aromatic moieties are hydrophobic. Examples of useful hydrophobic ether residues include but are not limited to, tolyl, hexyl, ethylphenyls, heptyl, cumyl, propylphenyls, octyl, butylphenyls, nonyl, phenylphenyls, pentylphenyls, decyl, isohexylphenyls, n-hexylphenyls, n-undecyl, heptylphenyls, lauryl, octylphenyls, isononylphenyls, nnonylphenyls, tetradecyl, decylphenyls, stearyl, n-tetradecylphenyls. hexadecylphenyls, and isooctadecylphenyls. Preferred hydrophobes are the nonylphenyl, dinonylphenyl, lauryl, and tridecyl groups.

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The use of the term "lower" to modify "alkyl" shall mean an alkyl group having from 1 to about 4 carbon atoms, e.g. methyl, ethyl, n-propyl, isopropyl, and tert-butyl. Further, the term "lower" when used to modify "aralkyl" shall mean an alkyl group having from 1 to about 4 carbon atoms substituted with a benzenoid radical, and the term "lower" when used to modify "acyl" shall mean a carbonyl terminated lower alkyl or lower aralkyl radical.

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Each of the A, A', and A" groups of formula VI preferably represent an ethylene, 1,2-propylene, 1,2-butylene unit or combinations thereof such that each of $(A-O)_a$ $(A'-O)_b$ and $(A''-O)_c$ is a water soluble, or water dispersable polyether group. The water solubility or water dispersability of a polyether group is a function of its molecular structure and/or its molecular weight. For example, an ethyleneoxy (EO) homopolymer having a molecular weight of

about 20,000 daltons or less is water soluble while a water soluble propyleneoxy (PO) homopolymer has a molecular weight of less than about 700 daltons. The structure of an EO-PO copolymer must be such that it contains at least about 50 wt % of ethyloxy groups to be water soluble. The structure-property relationships of EO and PO polyethers is described in the Encyclopedia of Polymer Science and Engineering, Second Edition, vol. 6, pp. 225-273, (John Wiley and Sons, Inc, 1986), while those of poly PO are described in vol. 6, page 300. In preferred compounds, the A, A', and A" groups consist essentially of ethylene groups, the value of b in formula VI above is preferably from about 2 to about 200, and the values of a and c preferably range from about 2 to about 50.

The above compounds are polymeric materials which can be made by any process within the purview of those having ordinary skill in the art. A preferred method is a two-step process, the first step of which comprises forming a mixture of compounds of the following formulas:

$$R^{1}$$
- $(OA')_{a}$ - OH + HO - $(A'-O)_{b}$ - H + HO - $(A''-O)_{c}$ - R^{6}

wherein all symbols are set forth above and under conditions which cause at least a portion of the terminal hydrogen atoms of the hydroxyl groups shown above to ionize leaving alkoxide oxygen atoms. These conditions can be brought about by adding to the mixture a strong base, for example an alkali or alkaline earth metal lower alkyl alkoxide, e.g. sodium methoxide. Of course, when B is an amino or amido group, the terminal hydroxyl of the compounds of formulas I, III, and IV should be replaced by an amine nitrogen having the appropriate substituents to introduce the desired B and R groups into the molecule. Examples of such amine functional compounds useful to introduce an amine group are the polyoxyethyleneamine and polyoxypropyleneamines (available under the tradename Jeffamine, from Texaco Chemical Company, Houston, Texas). Compounds of formula III and V, but wherein the terminal hydroxy is replaced by an amino nitrogen can be prepared by one of ordinary skill in the art. For example, compounds of formula III and V can be

subjected to a catalyzed ammoniation (with ammonia, or a lower alkylamine or lower acyl amide) for replacement of the hydroxyl, or to a capping of the hydroxyl with epichlorohydrin followed by ammoniation (with ammonia, or a lower alkylamine or lower acylamide) of the resulting glycidal group.

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The second step of the two-step process comprises forming a mixture of the product of step one in further admixture with a member selected from the group of a di-etherifying agent, a tri-etherifying agent, a di-esterifying agent, a tri-esterifying agent, and a mixture of two or more of such members. (Of course, when the compounds are amines or amides rather than hydroxyl compounds, the reaction is an alkylation or amidation reaction. To simplify the following description, references below to etherifying agents or esterifying agents in general should be construed as applicable to alkylating agents and amidifying agents, respectively.) This basic reaction can be represented by: $R^{1}-(OA')_{a}-OH + HO-(A'-O)_{b}-H + HO-(A''-O)_{c}-R^{6} + Y-R^{2}-(Y')_{d}-Y'' \rightarrow (VI)$

Ш IV

wherein Y, Y' and Y" are leaving groups in the case of etherifying agents or carboxy-functional groups in the case of esterifying agents. (Of course, the hydroxyl groups of the compounds of formulas III, IV, and V are amino or amido groups when B is to be such a linking group. Further, Y-R²-(Y')_a-Y" can also be an acetal, ketal, or orthoester, in which case Y and Y" are lower alkoxy groups which leave in a transacetalization, transketalization, or transorthoesterification, respectively. This leads to a compound of formula VI in which B is an ether linking group from these special classes of ethers, i.e. acetals, ketals or orthoesters.)

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It should be noted that when all B linkages are to be, for example, ether linkages, then only a di-etherifying agent and/or a tri-etherifying agent will be used to the exclusion of any esterifying agents. Likewise, when all B linkages are to be ester linkages, then only a di-esterifying agent and/or a triesterifying agent will be used to the exclusion of any etherifying agents. Similarly, if both d and e are to be zero (i.e. R² and R⁴ are only divalent radicals), then only a di-etherifying agent and/or a di-esterifying agent will be used to the exclusion of any a tri-etherifying agents and tri-esterifying agents.

Such etherifying (or alkylating) and esterifying (or amidifying) agents are capable of reacting with the hydroxyl (or amine or amide groups) or alkoxide oxygens of the reactants III, IV, and V above. These agents will thus introduce the divalent or trivalent radicals R² and R⁴ into the molecule. Examples of etherifying (or alkylating) agents are alkylhalides, e.g. divalent compounds (e.g. alpha, alpha'-dichloro-meta-xylene) that introduce a divalent R² and/or R⁴ group into the molecule, e.g. through the same mechanism as a classical Williamson ether (or amine alkylation) synthesis. When R² and/or R⁴ are to be aromatic radicals, it may be convenient to employ a di-halo-aromatic compound (e.g. di-bromo-benzene) which can be derivatized to the corresponding mono-Grignard reagent and reacted with the diol reactant of formula III, above (which will cap the diol with ether groups R² and/or R⁴ at each end of the diol to form, in the case of di-bromo-benzene, a bis-bromophenyl ether of the diol). This capped adduct can then be sequentially derivatized in a second Grignard reaction, the product of which can be reacted with reactants of formulas III and V, above, to give a compound of formula VI wherein R² and/or R⁴ are aromatic groups.

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Further examples of etherifying agents include epihalohydrin compounds, (e.g. those of the formula X-CH₂-CH-(O)-CH₂ wherein X is a leaving group, for example a halogen, e.g. chlorine which forms a chloride ion as the leaving group) or a precursor of an epihalohydrin (e.g. a compound of the formula X-CH₂-CH-(OR³)-CH₂-X', wherein X' is a leaving group). When this precursor is used, the epihalohydrin may be formed, at least in part, in situ, or the alkoxide moieties formed in step one may displace both the X and X' groups in an S_N2 reaction. When R^3 and/or R^5 are lower alkyl, then the epihalohydrin compound may be an ether having the formula X-CH₂-CH-(OR³)-CH₂-X', wherein X and X' are leaving groups and R^3 is a lower alkyl group (i.e. C_1 to C_4 alkyl, preferably methyl). Alternatively, the reaction mixture may also contain an alkylating agent of the formula X"- R^3 (e.g. methyl chloride or benzyl chloride) that can react with the alkoxide radical (or hydroxyl group) formed by opening of the oxirane ring of the epihalohydrin. This alkylating agent would preferably be added with the epihalohydrin

compound to reduce the opportunity of a side reaction with the alkoxide compounds which introduce the R^1 and R^6 groups into the molecule. Of course, if R^3 and R^5 are different, then a second epihalohydrin ether having the formula $X-CH_2-CH-(OR^5)-CH_2-X'$ and/or a second alkylating agent having the formula $X''-R^5$ must be employed to introduce the R^5 group into the molecule.

Examples of esterifying agents include di-basic and tri-basic organic acids, and reactive derivatives thereof, e.g. acid halides, acid anhydrides, and/or lower esters of such di-basic and tri-basic organic acids (all of which have carboxy-functional groups capable of reacting with the hydroxyl or alkoxide functional compounds of the formulas III, IV, V). The reaction conditions for the esterification reaction will of course differ from those appropriate for an etherification reaction. Esterification reactions with polybasic acids are discussed in the Encyclopedia of Polymer Science and Engineering, vol. 12, pp. 28-43 (John Wiley and Sons, Inc, New York, New York, 1988), the disclosure of which is incorporated herein by reference. The presence of ester linkages is less desirable when the compound will be used in aqueous compositions that are not at an essentially neutral pH (e.g. from a pH of about 6.5 to about 7.5). Compounds of formula VI wherein all B linkages are ether linkages are preferred for their resistance to hydrolysis.

The ratios of the reactants of formulas III, IV, and V may vary, but will generally range within 20 mole % to 45 mole % each of the compounds of formula III and V (if R¹ and R⁶ are the same, then the amount of the single reactant will, thus, be 40 mole % to 90 mole %) and 3 mole % to 60 mole %, preferably 10 mole % to 60 mole %, of the compound of formula IV. The amount of the etherifying or esterifying compound that is then reacted with the alkoxides may also vary, but will generally range from about 0.25:1 to about 1.5:1.0 (preferably about 0.8:1 to 1.2:1) equivalents of etherifying agent or esterifying agent (a divalent agent having two equivalents per mole) to hydroxyl equivalent weights of the reactants of formulas III (having one equivalent per mole), IV (having two equivalents per mole), and V (having one equivalent per mole).

It is believed that lubricating oils which contain predominantly compounds of formula VI, wherein R³ and/or R⁵ are not hydrogen, lower alkyl, or lower aralkyl, but are larger organic groups are superior for use in the practice of the invention. Such larger organic groups can result from the reaction of a second molecule of epichlorohydrin with, e.g., the intermediate alkoxide compound of the formula:

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 $R^{1}\text{-}(O\text{-}A')_{a}O\text{-}R^{2}\text{-}(O)\text{-}(O\text{-}(A'\text{-}O)_{b}\text{-}R^{4}\text{-}(OR^{5}))_{n}\text{-}O\text{-}(A''\text{-}O)_{c}\text{-}R^{6}$ and that this second molecule of epichlorohydrin can react, or may already have reacted, with the alkoxide $R^{1}\text{-}(O\text{-}A')_{a}\text{-}O$ (or $R^{6}\text{-}(O\text{-}A'')_{c}\text{-}O$). In this case, a compound will be formed in which R^{3} will then have the formula:

$$-R^2-(O)-(A'O)_a-O-R^1$$

which yields a molecule with significant branching in its molecular structure. Of course, such branching can also occur at R⁴ wherein R⁵ is similarly replaced by the reaction product of a second molecule of epichlorohydrin and an alkoxide. (If a tri-esterifying agent is use, then the branching will result from reaction of the third carboxyl group with one of the reactants of formulas III, IV, and V). This branching is believed to be beneficial to the performance of the molecule as a lubricating oil.

With respect to the reaction products comprising component B above, the linking agent of formula I is preferably epichlorohydrin although other epihalohydrins can be used. Also, trihaloalkanes can be used, such as 1,2,3-trichloropropane, 1,2,4-trichlorobutane, 1,3,6-trichlorohexane and the like. Instead of chlorine in the epihalohydrins and the trihaloalkanes, the corresponding bromine and iodine compounds can also be used, including compounds containing two or even three of the above halogens.

In the compounds of formula II, it is understood that EO stands for the residue of ethylene oxide and PO stands for the residue of propylene oxide and BO stands for the residue of butylene oxide.

When the X group of formula (II) is a mercapto group, the R⁷ group will preferably have from about 4 to about 36 carbon atoms, examples of which include but are not limited to alkoxylated dodecyl mercaptan and alkoxylated 1-hexadecanethiol.

The compounds of the formula (II) can be alkoxylated or non-alkoxylated secondary amines. When the compounds of formula II are secondary amines, h is a number from 0 to 50, preferably from 1 to 50, m is a number from 0 to 50 and p is a number from 0 to 50, preferably from 1 to 50. Examples of the secondary amines useful for the purposes of the invention include but are not limited to, alkoxylated dibutyl amine, alkoxylated dicyclohexyl amine, alkoxylated diethylethanolamine, and alkoxylated dioctylamine.

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The substituents that can be present on the substituted R⁷ and R⁸ groups can be single or multiple substitutions such as a halogen substitution, for example, Cl, Fl, I and Br: a sulfur functionality such as a mercaptan or thio group; a nitrogen functionality such as an amine or amide functionality; an alcohol functionality, a silicon functionality such as a siloxane; an ether functionality; or any combination thereof.

In general, compounds of formula II wherein the sum of n, m, and p is at least 1, especially at least 2, are preferred.

When R^7 is a secondary amino group, the group preferably contains from 4 to 22 carbon atoms.

Also, when X is hydrogen p is preferably a number of from 1 to 50. When R⁷ is a secondary amino group, p is preferably a number of from 1 to 50.

The nonoxy, nonthio, and nonamino components of the R⁷ group can be any substituted or unsubstituted, saturated or unsaturated organic moiety having from 1 to 36 carbon atoms (or from 2 to 36 carbon atoms when R⁷ is a secondary amino group). Thus, the nonthio, nonoxy, and nonamino components of the R⁷ aliphatic group can be linear or branched alkyl groups, linear or branched alkenyl or alkynyl groups, saturated carbocyclic moieties, unsaturated carbocyclic moieties having one or more multiple bonds, saturated heterocyclic moieties, unsaturated heterocyclic moieties having one or more multiple bonds, substituted linear or branched alkyl groups, substituted linear or branched alkenyl or alkynyl groups, substituted saturated carbocyclic moieties, substituted unsaturated carbocyclic moieties having one

or more multiple bonds, substituted saturated heterocyclic moieties, and substituted unsaturated heterocyclic moieties having one or more multiple bonds. Examples of the above include but are not limited to an alkyl group having from 4 to 22 carbon atoms, an alkenyl group having from 4 to 22 carbon atoms, and an alkynyl group having from 4 to 22 carbon atoms. R⁷ can also be an arenyl group. Arenyl groups are alkyl-substituted aromatic radicals having a free valence at an alkyl carbon atom such as a benzylic group. Alkyl groups having from 4 to 12 carbon atoms are preferred, and alkyl groups having from 8 to 10 carbon atoms are most preferred. The degree of ethoxylation is preferably from 2 to about 50 with the most preferred being from about 4 to about 50 while the degree of propoxylation and butoxylation can vary from 0 to about 50, preferably from 1 to about 10. The degree of propoxylation and or butoxylation will be determined by the desired degree of solubility or miscibility in the nonaqueous compositions of the invention. The solubility or miscibility will ultimately be determined by such factors as the number of carbon atoms in R⁷ and the relative amounts EO. PO and BO.

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Optionally, an additional component can be reacted with the linking agent of formula (I) and the compound of formula (II). A glycidyl ether or amine can be added to the reaction of formula (I) and formula (II). The amount of the glycidyl ether or glycidyl amine is from about 1 to about 20 mole percent based on the moles of formula (I) used in the reaction. When the glycidyl ether or glycidyl amine is added to the monofunctional starting material of formula II the ratio of formula I to formula II plus the glycidyl ether or glycidyl amine is preferably from about 0.8 to about 1.4. Examples of the glycidyl ethers include, but are not limited to, PEG 600 diglycidyl ether, TETRONICTM 701 tetraglycidyl ether, triglycidyl di or triethanolamine, polyoxyethylene (POE) 200 tallow amine diglycidyl ether, propoxylated (POP10) trimethylol propane triglycidyl ether, propoxylated (POP7) pentaerythritol tetraglycidyl ether. Examples of glycidyl amines include, but are not limited to, tetraglycidyl 1,6-hexane diamine, tetraglycidyl JEFFAMINETM EDR-148, and tetraglycidyl isophorone diamine.

The above reaction products can be obtained by the process disclosed in U.S. 5,827,453, which is expressly incorporated herein by reference.

The lubricating oils on the invention can comprise component A alone, component B alone, a mixture of components A and B in any proportions, e.g. from 1 to 99 mole %, preferably from 10 to 90 mole % of component A and from 99 to 1 mole %, preferably from 90 to 10 mole % of component B.

Alternatively, the above components or mixtures of components can be present in combination with one or more polyester lubricating oils in a mole ratio of from 99:1 to 10:90, preferably from 10:90 to 90:10.

The polyester lubricating oils include polyester obtained by reaction of

a) polyols with

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- b) fatty acids containing 6 to 22 carbon atoms, optionally in the presence of 0.05 to 8% by weight, based on the sum of components a) and b), of
- c) esters of thiocarboxylic acids corresponding to general formula(3) and/or (4):

$$R^1-S-R^3-COOH (3)$$

in which R¹, R², R³, and R⁴ may be the same or different and represent an alkyl, cycloalkyl, aryl or alkaryl group containing 1 to 22 carbon atoms.

Such polyesters are known from U.S. 4,919,828, which is incorporated herein by reference.

The polyols and the fatty acids of the polyesters may be saturated or olefinically unsaturated and may have a linear or branched carbon chain.

The substituents R¹ to R⁴ may be saturated or olefinically unsaturated, linear or branched where they are alkyl or cycloalkyl groups or the alkyl moiety of an alkaryl group.

The polyols are understood to be polyhydric alcohols containing at least two OH groups. Basically, there are no particular limitations to the chemical constitution of the polyols, i.e. they may be linear or even branched. The polyols are preferably selected from the group consisting of glycerol, trimethylol propane, neopentyl glycol and pentaerythritol.

The fatty acid components of the polyol fatty acid esters are preferably derived from fatty acids containing 8 to 18 carbon atoms which, in addition, are preferably saturated. The best effects are obtained when fatty acids containing 8 to 10 carbon atoms are used as the fatty acid component. These particular acids are known to the expert as caprylic acid, pelargonic acid and capric acid. These acids may be used either individually or in the form of mixtures. Mixtures of C_8 and C_{10} fatty acids are known as so-called head-fractionated fatty acids.

The lubricating oils of the invention alone or blended with polyesters exhibit excellent rheological properties, equivalent for example to known textile fiber lubricants. They are also biodegradable and are hence environmentally friendly.

The invention will be illustrated but not limited by the following examples.

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EXAMPLES

Example 1

This example will illustrate the production of a component A reaction product containing a compound of formula VI wherein B³ and B⁴ are amino groups. To a round bottom flask equipped with a stirrer, nitrogen inlet tube, and a distillation head, add 80 millimoles of nonylphenol ethoxylate (nominal 100 ethyleneoxy units per mole of ethoxylate) and 400 grams of toluene. To this mixture, add 80 millimoles of sodium hydroxide (as an aqueous solution at 50% by weight sodium hydroxide). Then heat the flask to azeotropically distill off most of the water with stirring and nitrogen gas sparging. Cool the solution to 80°C after which add 80 millimoles of epichlorohydrin. Allow to react until substantially all of the nonylphenol ethoxylate is capped with epichlorohydrin. Then add 20 millimoles of a polyethylene glycol having a molecular weight of about 6,000 grams/mole and amine terminated at each end (e.g. JEFFAMINE™ ED-6000). The reaction mixture is then maintained at 120°C until the epoxide titration reaches approximately zero. (A 4.0 gram aliquot of the reaction mixture + 4 grams of tetraethylammonium bromide can

be dissolved in 50 ml of glacial acetic acid and the resulting solution titrated with a 0.1036 N HClO₄ in a glacial acetic acid solution to methyl violet end point for the amount of epoxide (epoxy titration).

Example 2

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This example will illustrate the production of a component A reaction product containing a compound of formula VI wherein B³ and B⁴ are amido groups. To a round bottom flask equipped with a stirrer, nitrogen inlet tube, and a distillation head, add 80 millimoles of nonylphenol ethoxylate (nominal 100 ethyleneoxy units per mole of ethoxylate) and 400 grams of toluene. To this mixture, add 80 millimoles of sodium hydroxide (as an aqueous solution at 50% by weight sodium hydroxide). Then heat the flask to azeotropically distill off most of the water with stirring and nitrogen gas sparging. Cool the solution to 80°C after which add 80 millimoles of chloroacetic acid. Allow to react until substantially all of the nonylphenol ethoxylate is capped. Then add 20 millimoles of a polyethylene glycol having a molecular weight of about 6,000 grams/mole and amine terminated at each end (e.g. JEFFAMINE™ ED-6000). The reaction mixture is then maintained at 120°C until the reaction. reaches substantial completion. The reaction mixture can then be neutralized to a substantially neutral pH (about pH 7) with aqueous hydrochloric acid. Butoxytriglycol (BTG) and water can then be added.

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Example 3

This example illustrates the production of a component A reaction product containing a compound of formula VI wherein B³ and B⁴ are ether linkages. To a round bottom flask equipped with a stirrer, nitrogen inlet tube, and a distillation head, were added 70 millimoles of tridecyl alcohol ethoxylate (nominal 100 ethyleneoxy units per mole of ethoxylate), 30 millimoles of polyethylene glycol having a molecular weight of about 8,000 grams/mole and 400 grams of toluene. To this mixture was added 140 millimoles of sodium hydroxide (as an aqueous solution at 50% by weight sodium hydroxide). The flask was then heated to azeotropically distill off most of the water with stirring

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and nitrogen gas sparging. The conditions of distillation were such that about 1,000 ppm of water remained in the toluene solution. The solution was then cooled to 80°C after which 90 millimoles of epichlorohydrin were added. The reaction mixture was then maintained at 80°C until the epoxide titration reached approximately zero. (A 4.0 gram aliquot of the reaction mixture and 4 grams of tetraethylammonium bromide can be dissolved in 50 ml of glacial acetic acid and the resulting solution titrated with a 0.1036 N HCIO₄ in glacial acetic acid solution to a methyl violet end point for the amount of epoxide (epoxy titration)).

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Example 4

The reaction was run according to the procedure outlined in Example 3 with the following exceptions. The amount of tridecyl alcohol ethoxylate was 80 millimoles, the amount of polyethylene glycol was 20 millimoles, and the amount of epichlorohydrin was 90 millimoles. In addition, 130 millimoles of sodium methoxide was used in place of the sodium hydroxide and then methanol was distilled off.

Example 5

The reaction was run according to the procedure outlined in Example 3 with the following exceptions. The amount of tridecyl alcohol ethoxylate was 85 millimoles, the amount of polyethylene glycol was 15 millimoles, and the amount of the sodium hydroxide was 130 millimoles.

Example 6

The reaction was run according to the procedure outlined in Example 4 with the following exceptions. The amount of tridecyl alcohol ethoxylate was 85 millimoles, the amount of polyethylene glycol was 15 millimoles, the amount of sodium methoxide was 130 millimoles, and the amount of the epichlorohydrin was 115 millimoles.

Example 7

The reaction was run according to the procedure outlined in Example 4 with the following exceptions. The tridecyl alcohol ethoxylate was replaced with 80 millimoles of an ethoxylate of mixed alcohols having 12, 13, and 14 carbon atoms (nominal degree of ethoxylation of 100 moles of ethylene oxide per mole of alcohol) and the amount of polyethylene glycol was 20 millimoles.

Example 8

The reaction was run according to the procedure outlined in Example 4 with the following exceptions. The tridecyl alcohol ethoxylate was replaced with 80 millimoles of an ethoxylate of mixed alcohols having 8, 9 and 10 carbon atoms (nominal degree of ethoxylation of 100 moles of ethylene oxide per mole of alcohol) and the amount of polyethylene glycol was 20 millimoles.

Example 9

The reaction was run according to the procedure outlined in Example 4 with the following exceptions. The tridecyl alcohol ethoxylate was replaced with 80 millimoles of a nonyl phenol ethoxylate (nominal degree of ethoxylation of 100 moles of ethylene oxide per mole of alcohol) and the amount of polyethylene glycol was 20 millimoles.

Example 10

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This example will illustrate the use of meta-alpha, alpha'-dichloromethyl benzene to introduce the meta-xylyl group into the structure of the compound of formula VI in the component A reaction product. To a 250 ml round bottom flask equipped with a stirrer, nitrogen inlet tube, and a distillation head were added 65 parts of tridecyl alcohol ethoxylate (nominal 100 ethyleneoxy units per mole of ethoxylate) and 18.5 parts by weight of polyethylene glycol having a molecular weight of about 8,000 grams/mole and 82 parts by weight of toluene (the mixture having a hydroxyl equivalent of 4.06). The mixture was heated to azeotropically distill off the water with stirring +N₂ sparge. After the water concentration was less than 50 ppm the

mixture was cooled to 90°C. Sodium methoxide was added in an amount of 4.1 parts by weight of 25% sodium methoxide in methanol such that OH:NaOMe = 1:1 based on the calculated hydroxyl value of the mixture. Heat was applied to distill off formed methanol (by distilling off about half of the initial weight of toluene from the flask). The reaction mixture was then refluxed for 1 hour. The flask was cooled to 80°C and 1.64 parts by weight of meta-dichloromethyl benzene was added. After about ten minutes, an additional 0.2 parts by weight of meta-dichloromethyl benzene was added. The reaction mixture was maintained at 110°C for about 1 hour then allowed to stand at room temperature for 16 hours before being reheated to 110°C for about 2 more hours. The remaining toluene was then vacuum stripped.

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Example 11

This example will illustrate the use of dimethyl maleate to introduce an ester linkage into the structure of the compound of formula VI in the component A reaction product. To a 250 ml round bottom flask equipped with a stirrer, nitrogen inlet tube, and a distillation head were added 86 parts to tridecyl alcohol ethoxylate (nominal 100 ethyleneoxy units per mole of ethoxylate) and 15.6 parts by weight of polyethylene glycol having a molecular weight of about 8,000 grams/mole and 20 parts by weight of toluene (the mixture having a hydroxyl equivalent of 1.8). To this mixture was added 1.8 parts by weight of dimethyl maleate. The mixture was then heated to 100°C to azeotropically distill off any water with stirring +N₂ sparge. Then 0.1% of a commercial esterification catalyst, FASCATTM 4100, M&T Chemicals, Rahway, New Jersey, was added and the mixture was heated to 170°C for two hours.

This maleate ester was then converted to a sulfosuccinate ester by reaction with metabisulfite. To perform this reaction, the cooled reaction product from above was mixed with 100 parts by weight of deionized water and then 1.14 parts by weight of $Na_2S_2O_5$ were added. The progress of the reaction was determined by titration with iodine and was quenched at about 92% conversion.

Example 12

This example illustrates the preparation of a component B reaction product.

About 150 grams of decyl alcohol ethoxylated with an average of 4 moles of ethylene oxide (0.45 OH equivalents) were mixed with 385 grams of toluene and 54 grams of 50% aq NaOH (0.675 equivalents). The water was removed by azeotropic distillation and when a moisture level of less than 0.8% was reached, about 46 grams (0.51 equivalents) of epichlorohydrin were slowly added. This mixture was allowed to react at 100-110°C for 24 hours. This mixture was then removed and filtered to remove the NaCl and vacuum stripped to remove the toluene to give an amber, easily pourable liquid product that was dispersible in water.

Example 13

This example also illustrates the preparation of a component B reaction product.

About 51 grams of butanol ethoxylated with an average of 2 moles of ethylene oxide (0.32 OH equivalents) were mixed with 120 grams of toluene and 25 grams of 50% aq NaOH (0.32 equivalents). The water was removed by azeotropic distillation and when a moisture level of less than 0.8% was reached, about 46 grams (0.24 equivalents) of epichlorohydrin were slowly added. This mixture was allowed to react at 100-110°C for 24 hours. This mixture was then removed and filtered to remove the NaCl and vacuum stripped to remove the toluene to give an amber, easily pourable liquid product that was insoluble in water.

25 Example 14

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This example further illustrates the preparation of a component B reaction product.

About 200.0 gm (0.654 hydroxyl equivs.) of octyl alcohol ethoxylated with an average of 4 moles of ethylene oxide was mixed with 400gm toluene

and 78.4gm (0.98 equivs.) of 50% NaOH. Water was removed by azeotropic distillation until the level was below 0.8%. The mixture was cooled to 80°C and 67.2gm (0.72 moles) of epichlorohydrin was added over 45 mins. The mixture was stirred for 24 hrs at 110°C until the epoxy titration showed no epoxide left. The material was cooled, filtered and the toluene was removed by vacuum distillation leaving a dark brown low viscosity liquid.

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What is claimed is:

1. A method for reducing friction and wear between solid surfaces in relative motion comprising applying to at least one of said solid surfaces a lubricating oil comprising

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A. at least one compound which is the reaction product under basic conditions of the following reactants:

a) at least one member selected from the group consisting of R¹(O-A)_aOH and R¹(O-A)_aNH₂ (III);

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- b) at least one member selected from the group consisting of $R^6(OA'')_cOH$ and $R^6(OA'')_cNH_2$ (V);
- c) at least one member selected from the group consisting of $HO(A'O)_{b}H$ and $H_{2}N(A'-O)_{n}A'NH_{2}$ (IV);
- d) at least one linking compound of the formula $YR^2-(Y')_d-Y''$; and

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e) optionally a compound of the formula R⁵Y'" and R³Y"" wherein

R¹ and R⁶ are monovalent hydrophobic groups having from 4 to about 50 carbon atoms, independently selected from the group consisting of an aliphatic group, an aromatic group, and an aralkyl group;

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R² is selected from the group consisting of aliphatic, substituted aliphatic, aromatic, or substituted aromatic groups, each group being divalent or trivalent;

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R³ and R⁵ are independently selected from hydrogen, lower alkyl, lower aralkyl; or a larger organic group resulting from the reaction of a second molecule of the component d) linking compound:

Y, Y', Y", are independently selected from the group consisting of halo, epoxy and carboxyl, Y'" and Y"" are selected from the group consisting of halo and hydroxyl;

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each of a, b, c, d, and n are integers, wherein each of a and c is independently any integer from 0 to about 200; b is any integer from 0 to about 450; d is zero or 1; and n is any integer from 0 to about 450; and

each of A, A', and A" is independently an alkylene group containing from 2 to 36 carbon atoms; and/or

B. at least one compound which is the product of the reaction between compounds comprising a linking agent of formula I

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$$R(Y)_3 (I)$$

wherein each Y group is a halogen atom or one Y group is a halogen atom and two Y groups with two adjacent carbon atoms in the R group and an oxygen atom form an epoxy group, and R is an alkanetriyl group containing from 3 to 10 carbon atoms; and a compound having the formula II

$$R^{7}(EO)_{n}(PO)_{m}(BO)_{n}X$$
 (II)

wherein R⁷ is a substituted or unsubstituted, saturated or unsaturated, organic oxy or thio group having from 1 to 36 carbon atoms or a secondary amino group having from 2 to 36 carbon atoms; n is a number of from 0 to 50, e.g., from 1 to 50; m is a number of from 0 to 50 e.g., from 1 to 50; p is a number of from 0 to 50 e.g., from 1 to 50; and X is hydrogen, or X can be a mercapto group or an amino group in place of a terminal -OH group, provided that when X is mercapto or amino; the sum of n, m, and p must be at least 1, and the mole ratio of I:II is from about 0.2:1 to about 5:1.

- 2. The method of claim 1 wherein the lubricating oil also contains a polyester lubricant in a mole ratio of from about 99:1 to about 10:90.
- 3. The method of claim 1 wherein the lubricating oil is added to textile fibers to reduce fiber-to-metal friction during processing.
 - 4. The method of claim 2 wherein the lubricating oil of claim 2 is added to textile fibers to reduce fiber-to-metal friction during processing.
 - 5. The method of claim 1 wherein the reaction product in component A contains at least one compound of formula I:

$$R^{1}$$
- $(O-A)_{a}$ - B^{1} - R^{2} - $(B^{2}$ - $R^{3})_{d}$ - $(B^{3}$ - $(A'-O)_{b-f}$ - $(A'-B^{4})_{f}$ - R^{4} - $(B^{5}$ - $R^{5})_{e})_{n}$ - B^{6} - $(A''O)_{c}$ - R^{6} (I) wherein:

R¹ and R⁶ are monovalent hydrophobic groups independently selected from the group consisting of an aliphatic group, a substituted aliphatic group, an aromatic group, and a substituted aromatic group;

R² and R⁴ are independently selected from the group consisting of aliphatic, substituted aliphatic, aromatic, or substituted aromatic groups, each group being divalent or trivalent;

R³ and R⁵ are independently selected from hydrogen, lower alkyl and lower aralkyl, and -R²-(O)-(A'O)_a-O-R¹;

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B¹, B², B³, B⁴, B⁵, and B⁶ are linking groups independently selected from the group consisting of an oxygen atom, a carboxylate group, an amino group, and an amido group;

each of a, b, c, d, e, f, and n are integers, wherein each of a and c are independently any integer from 0 to about 200; b is any integer from 0 to about 450; d, e, and f are zero or 1; and n is any integer from 0 to about 450; and each of A, A', and A" is independently an alkylene group containing from 2 to 36 carbon atoms.

- 6. The method of claim 5 wherein R² and R⁴ are independently selected from the group consisting of alkanetriyl groups having from 2 to 10 carbon atoms and aralkylene groups having one benzenoid ring and from 1 to 10 aliphatic carbon atoms.
 - 7. The method of claim 5 wherein each of B¹, B², B³, B⁴, B⁵, and B⁶ is an oxygen atom.
- 20 8. The method of claim 5 wherein each of B¹, B², B³, B⁴, B⁵, and B⁶ is a carboxylate group.
 - 9. The method of claim 5 wherein f is 1 and each of B¹, B², B³, B⁴, B⁵, and B⁶ is an amino group or an amido group having the formula -N(R)-, wherein R is selected from the group consisting of hydrogen, lower alkyl, and lower acyl.
- 10. The method of claim 5 wherein d and e are each 1 and R² and R⁴ are alkanetriyl groups having from 2 to 10 carbon atoms.

11. The method of claim 5 wherein each of R¹ and R⁶ is independently an aliphatic or aralkyl group having from 10 to about 30 carbon atoms.

- 12. The method of claim 5 wherein each of d and e is 1 and each of R³ and R⁵ are hydrogen, methyl, or benzyl.
- 5 13. The method of claim 5 wherein A, A' and A" are ethylene.
 - 14. The method of claim 5 wherein each of a and c is independently from about 2 to about 50.
 - 15. The method of claim 5 wherein b is from 2 to about 200.
 - 16. The method of claim 5 wherein n is an integer of from 2 to about 20.
- 17. The method of claim 5 wherein R¹ and R⁶ are the same and are selected from the group consisting of alkyl groups having from about 8 to about 15 carbon atoms and alkylphenyl groups wherein the alkyl groups substituted on the phenyl have from about 6 to about 12 carbon atoms.
- 18. The method of claim 5 wherein each of R¹ and R⁶ is independently an aliphatic or aromatic group having from 10 to about 30 carbon atoms; R² and R⁴ are both alkanetriyl groups having from 2 to 10 carbon atoms; d and e are each 1; R³ and R⁵ are hydrogen, methyl or benzyl; f is zero; each of B¹ B⁶ is an oxygen atom; each of A, A′, and A″ is ethylene; a and c are independently from 2 to about 50; b is from 2 to about 200; and n is an integer of from 2 to about 200.
 - 19. The method of claim 18 wherein R² and R⁴ are both propanetriyl groups.
 - 20. The method of claim 5 wherein each of R¹ and R⁵ is independently an aliphatic or aromatic group having from 10 to about 30 carbon atoms; d, e, and f are each zero; each of B¹ B⁶ is an oxygen atom; each of A, A', and A" is

ethylene; a and c are independently from 2 to about 50; b is from 2 to about 200; and n is 1.

- 21. The method of claim 20 wherein R² and R⁴ are both meta-xylyl groups.
- 22. The method of claim 1 wherein the reaction product in component A is formed from a mixture in which the reactants of the formula III, IV, and V are from a 20 mol % to 45 mol % each of the compounds of formula III and V and 3 mol % to 60 mol % of the compound of formula IV.
- 23. The method of claim 1 wherein component A d) is epichlorohydrin.
- 24. The method of claim 23 wherein the mole ratio of epichlorohydrin to (III) is from about 0.80/1 to about 2/1.
 - 25. The method of claim 1 wherein component B is at least one compound which is the reaction product of an epihalohydrin and a compound of the formula VII

 $R^{8}(EO)_{n}(PO)_{m}OH$ VII

wherein R⁸ is a substituted or unsubstituted, saturated or unsaturated aliphatic oxy group having from 4 to 22 carbon atoms; n is a number from 0 to 50 and m is a number from 0 to 50; wherein the mole ratio of epihalohydrin to (VII) is from about 0.60/1 to about 5/1.

- 26. The method of claim 1 wherein in component B, R⁷ is an alkoxy group having from 4 to 12 carbon atoms.
- 27. The method of claim 1 wherein in component B, R⁷ is an alkoxy group having from 8 to 10 carbon atoms.
- 28. The method of claim 1 wherein in component B, the linking agent is epichlorohydrin.

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29. The method of claim 1 wherein in component B, n is a number from 2 to about 20.

- 30. The method of claim 1 wherein in component B, the mole ratio of linking agent to (II) is from about 0.80/1 to about 2/1.
- 5 31. The method of claim 1 wherein in component B, R⁷ is an alkoxy group having from 4 to 12 carbon atoms.
 - 32. The method of claim 31 where R⁷ is an alkoxy group having from 8 to 10 carbon atoms and n is a number from 2 to about 20.
 - 33. A lubricating oil composition comprising
 - A. at least one compound which is the reaction product under basic conditions of the following reactants:
 - a) at least one member selected from the group consisting of R¹(O-A)_aOH and R¹(O-A)_aNH₂ (III);
 - b) at least one member selected from the group consisting of $R^6(OA'')_cOH$ and $R^6(OA'')_cNH_2$ (V);
 - c) at least one member selected from the group consisting of $HO(A'O)_bH$ and $H_2N(A'-O)_nA'NH_2$ (IV);
 - d) at least one linking compound of the formula $YR^2-(Y')_d-Y''$; and
 - e) optionally a compound of the formula R⁵Y'" and R³Y""

wherein:

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R¹ and R⁶ are monovalent hydrophobic groups having from 4 to about 50 carbon atoms, independently selected from the group consisting of an aliphatic group, an aromatic group, and an aralkyl group;

R² is selected from the group consisting of aliphatic, substituted aliphatic, aromatic, or substituted aromatic groups, each group being divalent or trivalent;

R³ and R⁵ are independently selected from hydrogen, lower alkyl, lower aralkyl, or a larger organic group resulting from the reaction of a second

molecule of the component d) linking compound;

Y, Y', Y", are independently selected from the group consisting of halo, epoxy and carboxyl, Y'" and Y"" are selected from the group consisting of halo and hydroxyl;

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each a, b, c, d, and n are integers, wherein each of a and c is independently any integer from greater than 20 to about 200; b is any integer from 0 to about 450; d is zero or 1; and n is any integer from 0 to about 450; and

each of A, A', and A" is independently an alkylene group containing from 2 to 36 carbon atoms; and/or

B. at least one compound which is the product of the reaction between compounds comprising a linking agent of formula I

$$R(Y)_3 \tag{I}$$

wherein each Y group is a halogen atom or one Y group is a halogen atom and two Y groups with two adjacent atoms in the R group and an oxygen atom form an epoxy group, and R is an alkanetriyl group containing from 3 to 10 carbon atoms, and a compound having the formula (II)

$$R^{7}(EO)_{n}(PO)_{m}(BO)_{p}X \tag{II}$$

wherein R⁷ is a substituted or unsubstituted, saturated or unsaturated, organic oxy or thio group having from 1 to 38 carbon atoms or a secondary amino group having from 2 to 36 carbon atoms; n is a number from 0 to 50, e.g., from about 1 to 50; m is a number of from 0 to 50, e.g., from 1 to 50; p is a number of from 0 to 50, e.g., from 1 to 50; and X is hydrogen, or X can be a mercapto group or an amino group in place of a terminal -OH group, provided that when X is mercapto or amino; the sum of n, m, and p must be at least 1, and the mole ratio of I:II is from about 0.2:1 to about 5:1; and

- C. A polyester lubricating oil; wherein the mole ratio of A + B to C is from about 99:1 to about 10:90.
- 34. The composition of claim 33 wherein component C is at least one polyester obtained by reaction of
 - a) polyols with
 - b) fatty acids containing 6 to 22 carbon atoms, optionally in the

presence of 0.05 to 8% by weight, based on the sum of components a) and b), of

c) esters of thiocarboxylic acids corresponding to general formula(3) and/or (4):

R¹-S-R³-COOH

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(3)

HOOC-R³-S-R⁴-COOH

(4)

in which R¹, R², R³, and R⁴ may be the same or different and represent an alkyl, cycloalkyl, aryl or alkaryl group containing 1 to 22 carbon atoms.

35. The composition of claim 33 wherein component B is at least one compound which is the reaction product of an epihalohydrin and a compound of the formula VII

$$R^{8}(EO)_{n}(PO)_{m}OH$$
 (VII)

wherein R⁸ is a substituted or unsubstituted, saturated or unsaturated aliphatic oxy group having from 4 to 22 carbon atoms; n is a number from 0 to 50 and m is a number from 0 to 50; wherein the mole ratio of epihalohydrin to (VII) is from about 0.60/1 to about 5/1.

- 36. The composition of claim 33 wherein component A d) is an epihalohydrin.
- 37. A textile spinning finish which is an aqueous solution or dispersion comprising, as nonaqueous ingredients,
 - from about 35 to about 100% by weight of a lubricant which is component (I) of claim 33 or the lubricating oil composition of claim 33; and
 - ii) from 0 to about 65% by weight of emulsifiers, antistatic agents, wetting agents and/or additives.

INTERNATIONAL SEARCH REPORT

International application No. PCT/US00/28750

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) :C10M 107/20, 107/40 US CL : 508/223, 225, 452, 454, 455, 457, 458, 543, 575 : 252/8.81			
According to International Patent Classification (IPC) or to both national classification and IPC			
B. FIELDS SEARCHED			
Minimum documentation searched (classification system followed by classification symbols)			
U.S. : 508/223, 225, 452, 454, 455, 457, 458, 543, 575 : 252/8.81			
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched			
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)			
East 1.1 West 2.0			
C. DOCUMENTS CONSIDERED TO BE RELEVANT			
Category*	Citation of document, with indication, where app	propriate, of the relevant passages	Relevant to claim No.
A	US 4,252,745 A (KWONG et al) 24 Fe 59	bruary 1981, col2, lines 20-	1-37
Y	US 5,370,810 A (EMERT et al) 06 December 1994, col. 4, lines 1-19, col. 4, lines 42-65		1-37
A	US 5, 382, 372 A (EICKEN et al) 17 January 1995, col.2, lines 27-37		37
A	US 5,506,332 A (FUNHOFF et al) 09 April 1996, col.2, lines 23-54		1-37
Y	US 5,723,417 A (KITAHARA et al) 03 March 1998, see entire document		1-37
A	US 5,916,854 A (INAYA et al) 29 June 1999, col. 6, lines 21-59		1-37
Further documents are listed in the continuation of Box C. See patent family annex.			
Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention			lication but cited to understand
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"P" document published prior to the international filing date but later than "&" document member of the same patent family the priority date claimed			
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