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LUBRICATING FILMS

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The present invention is broadly concerned with a novel class of lubricity additives, additive concentrates, and oleophilic liquid compositions containing these mixtures. The invention is more specifically concerned with improving the lubricity of hydrocarbon liquids such as gasolines, aviation turbo fuel, kerosene, diesel fuel, lubricating oil and mineral lubricating oils. Other base fluids include liquid carbohydrates and esters such as dioctyl sebacate and didecyl adipate. The present invention also contemplates the use of the lubricity additives in solid products such as paraffin wax, lubricating grease and Carbowax. The invention in one specific aspect relates to improving the lubricity of middle distillates, particularly jet fuels.

Many oil compositions are designed for lubricating under boundary conditions (e.g. crankcase oils, aviation oils and gear oils) where the prevention of wear of the metal surfaces under heavy loading is a serious problem. One common example of such heavy loading occurs in the operation of the valve lifter mechanism of gasoline engines. Here, pressures of 50,000 to 100,000 p.s.i. can occur between the valve lifter and its actuating cam, and metal wear is accordingly high.

Another objective of the present invention is to improve the lubricity of distillate fuels boiling in the range from about 50° to 750° F. Such fuels include aviation turbo-jet fuels, rocket fuel (MIL-R-25576B), kerosenes, diesel fuels, and heating oils. Aviation turbo-jet fuels in which the additives may be used normally boil between about 50° and about 550° F. and are used in both military and civilian aircraft. Such fuels are more fully defined by U.S. Military Specifications MIL-F-5624F, MIL-F-2565A, MIL-F-25554A, MIL-F-25558B, and amendments thereto, and in ASTM D-1655-62T. Kerosenes and heating oils will normally have boiling ranges between about 300° and about 750° F. and are more fully described in ASTM Specification D-396-48T and supplements thereto, where they are referred to as No. 1, and No. 2 fuel oils. Diesel fuels in which the additives be may employed are described in detail in ASTM Specification D-975-35T and later versions of the same specification. These additives may be used in metal working fluids in machining.¹

The additives of the present invention may also be employed in conjunction with a variety of other additives commonly used in fuels such as those set forth above. Typical of such additives are rust inhibitors, anti-emulsifying agents, corrosion inhibitors, anti-oxidants, dispersants, dyes, dye stabilizers, haze inhibitor, antistatic agents and the like. It will frequently be found convenient to prepare additive concentrates for use in the various types of fuels and thus add all of the additives simultaneously.

Broadly, the additives of the present invention may be classified as:

(I) Mixtures of compounds X and Y in a carrier fluid, and

(II) Reaction products of X and Y in a carrier fluid.

Where:

X=M(OR)_n and Y=an organic polyol or polyamine, and where:

¹ E.g. machining and lubrication of steel and ferrous alloys, aluminum alloys, titanium, brass, stainless steel, etc.

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M=Ti or other transition elements such as Hf, Ce, V, Nb, Fe and V; a Group IV element such as Si, Ge, Sn or Pb; B or Al (Group III elements); or a Group V element such as P, As, Sb or Bi.

R=a monovalent alkyl group containing from 1 to 12 and preferably from 1 to 6 carbon atoms (e.g. —CH₃, —C₂H₅, —C₃H₇, —C₆H₁₃)

n=2 or greater, depending upon the valence of M, and preferably 3 or 4.

It is preferred that M=Ti, Si, B and P. Y=a polyol (e.g. a glycol, HO—R'—OH) or a polyamine (e.g. a diamine, H₂N—R'—NH₂) where R' is an organic radical containing 8 to 40, and preferably 20 to 36, carbon atoms.

Specific examples of M(OR)_n are Ti(OC₂H₅)₄, tetraethyl orthotitanate; Ti(OC₄H₉)₄, tetrabutyl orthotitanate; Si(OC₂H₅)₄, tetraethyl orthosilicate; Si(OC₆H₁₃)₄, tetrahexyl orthosilicate; B(OC₄H₉)₃, tributyl borate; B(OC₈H₁₇)₃, trioctyl borate; P(OC₂H₅)₃, triethyl phosphite; and P(OC₄H₉)₃, tributyl phosphite.

It is recognized that some alkoxides are monomer only under special conditions (e.g. very dilute solution). For example, Ti(OC₂H₅)₄, Ti(OC₃H₇)₄ and Ti(OC₄H₉)₄ are trimeric, Ti₃(OR)₁₂. Consequently, it is understood that M(OR)_n in this invention may be replaced by (M(OR)_n)_x where x is greater than 1.

Specific examples of polyols are, for example, ethylene glycol; 1,4-butane diol; 1,5-pentane diol; 1,2,6-hexane triol; C₃₆ glycol made from C₃₆ dilinoleic acid; C₄₀ glycol made by reacting ethylene glycol and C₃ dilinoleic acid; esters of sorbitol and fatty acids and which still contain two or more hydroxy groups (e.g. sorbitan monooleate); polypropylene glycol; 1,4-cyclohexane dimethanol; and C₁₆ glycol made by the aldolization of iso-octyl aldehyde.

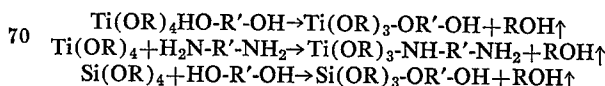
Specific polyamines are, for example, triethylene tetramine; tetraethylene pentamine; dimer triamine, dimer diamine and dimer tetramine made from C₃ dilinoleic acid; imino-bis-propyl amine; 1,6-hexane diamine; and p-phenylene diamine.

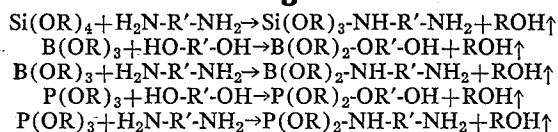
In place of polyols or polyamines, compounds having both a hydroxy group (—OH) and an amine group (—NH₂) may be used. Examples of these compounds are alkanolamines such as monoethanolamine, N-aminoethyl ethanolamine and polyglycolamines (e.g.



The specific structures chosen for compounds X and Y will depend, among other things, on the carrier fluid to be used and whether or not a solution—rather than colloidal dispersion—of the compound(s) is desired. For example, if a hydrocarbon such as kerosene or mineral oil is to be used as the carrier fluid and if solubility is desired, then the preferred polyols and polyamines would be the C₃₀ to C₄₀ compounds derived from C₃₆ dilinoleic acid. Secondly, if one of the compounds (either X or Y) is of borderline or poor solubility in the carrier fluid, X and Y may be partially reacted first before addition to the carrier. Furthermore, the reaction product of X and Y is frequently more effective than the mixture of X and Y in reducing wear and scuffing. It is believed that this is due to the fact that when only one species is involved, adsorbed layers contain equal amounts of the X and Y structural features, each of which is important. On the other hand, with a mixture, one compound may be so poorly or weakly adsorbed on a surface (e.g. metal) that it does not take part in the protection of the surface.

The reaction products may be prepared as follows:





sulfonic acid were used as a catalyst. The 2 phase mixture slowly became 1 phase while refluxing at 85° to 90° C. and 9.8 ml. ethanol (theory=10.6 ml.) were collected in about 1 hour. The product was a clear water-white liquid. At 1% in mineral oil, the blend was hazy. It was nevertheless tested in the ball-on-cylinder machine.

TABLE II

Additives in mineral oil ¹	Percent metallic contact ²			Coeff. of friction ²		
	240 g.	1,000 g.	4,000 g.	240 g.	1,000 g.	4,000 g.
None.....	85	93	99	0.103	0.093	0.085
1% tetraethyl-o-silicate/ethylene glycol product.....	9	1	2	0.071	0.046	0.062
1% tetraethyl-o-silicate.....	6	31	100	0.109	0.101	0.105
1% tetraethyl-o-silicate/sorbitan monooleate reaction product.....	74	82	99	0.090	0.065	0.078

¹ Paraffinic distillate oil: Vis. Saybolt sec. 100 at 100° F.; vis. index 90-110; boiling range 650° F. to 800° F.
² Ball-on-cylinder tests, steel-on-steel (AISI 52100) 240 r.p.m., 32 minutes. The apparatus used is described in the Journal of the American Society of Lubrication Engineers, entitled "ASLE Transactions," vol. 4, pages 1-11 in 1961. "ASLE" is American Society of Lubrication Engineers. In essence, the system consists basically of a fixed metal ball loaded against a rotating cylinder. The extent of metallic contact is determined by measuring both the instantaneous and average electrical resistance between two surfaces. The apparatus is described in U.S. Patent 3,129,580 issued May 21, 1964, entitled "Apparatus for Measuring Friction and Contacts Between Sliding Lubricating Surfaces"; Inventors: Furey et al.

In order to further illustrate the invention, the following examples are given:

EXAMPLE 1

Table I summarizes the results of ball-on-cylinder tests using combinations of tetraethyl-orthosilicate, (EtO)₄Si, and dimer tetramine and dimer diamine. These are not reaction products but simply mixtures.

Table II shows that the tetraethyl-o-silicate/ethylene glycol monoester is extremely effective in reducing metallic contact over the entire load range. It is also effective as an antifriction additive. A similar monoester made with sorbitan monooleate as the polyol, however, is much less effective. This suggests that lower molecular weight glycols or polyols are preferred.

TABLE I

Additives in mineral oil ¹	Percent metallic contact ²			Coeff. of friction ²		
	240 g.	1,000 g.	4,000 g.	240 g.	1,000 g.	4,000 g.
None.....	85	93	99	0.103	0.093	0.085
0.5% tetraethyl-o-silicate.....	0	0	0	0.055	0.066	0.085
0.5% dimer tetramine.....	6	31	100	0.109	0.101	0.105
1% tetraethyl-o-silicate.....	1	12	99	0.043	0.063	0.080
1% dimer tetramine.....	12	7	100	0.117	0.091	0.089
0.5% tetraethyl-o-silicate.....						
0.5% dimer diamine.....						

¹ Paraffinic distillate oil: Vis. Saybolt sec. 100 at 100° F.; vis. index 90-110; boiling range 650° F. to 800° F.
² Ball-on-cylinder tests, steel-on-steel (AISI 52100), 240 r.p.m., 32 minutes, 77° F. oil temperature. The apparatus used is described in the Journal of the American Society of Lubrication Engineers, entitled "ASLE Transactions," vol. 4, pages 1-11 in 1961. "ASLE" is American Society of Lubrication Engineers. In essence, the system consists basically of a fixed metal ball loaded against a rotating cylinder. The extent of metallic contact is determined by measuring both the instantaneous and average electrical resistance between two surfaces. The apparatus is described in U.S. Patent 3,129,580 issued May 21, 1964, entitled "Apparatus for Measuring Friction and Contacts Between Sliding Lubricating Surfaces"; Inventors: Furey et al.

It can be seen from Table I that a combination of (EtO)₄Si and dimer tetramine is extremely effective in reducing metallic contact at all loads tried—even at 4000 g. (141,000 p.s.i. mean Hertz pressure). Metallic contact is reduced to zero. This is even better than the metal dithiophosphates which tend to act only at the higher load. Neither tetraethyl-o-silicate nor the tetramine alone at the same total concentration (1 wt. percent) has any effect at the highest load (4000 g.). They do, however, show some benefits at lower loads—and the tetramine alone reduces friction. However, only the combination produces low metallic contact as well as low friction over the entire load range.

Table I also shows that the tetramine combination is much preferred over combinations with either dimer diamine.

EXAMPLE 2

In another approach, tetraethyl-o-silicate was reacted with ethylene glycol to form a monoester as described. 0.2 mole (41.6 g.) of the silicate and 0.2 mole (12.4) of ethylene glycol were placed in a 250 ml., 2 neck flask containing boiling chips and a magnetic stirrer and a side arm to collect ethanol. A few crystals of p-toluene

EXAMPLE 3

Two derivatives of triethyl borate were prepared and evaluated in the ball-on-cylinder device. One was made by reacting the borate with ethylene glycol. The other was made by using sorbitan monooleate as the polyol.

Preparation of (RO)₃B/polyol monoesters

A. Triethyl borate+ethylene glycol.—0.1 mole (EtO)₃B (15.6 g.)+0.1 mole ethylene glycol (6.2 g.) was heated in flask with no solvent until theoretical (0.1 mole) ethanol was collected. The reaction took 15 minutes at 85° C., resulting in a clear, water-white fluid. 1% in mineral oil produces a hazy blend.

B. Triethyl borate+sorbitan monooleate.—0.1 mole (EtO)₃B (15.6 g.)+0.1 mole sorbitan monooleate was heated in flask with no solvent until 6 ml. ethanol collected (theoretical amount is 5.3 ml.). Refluxing occurred when the liquid temperature reached 110° to 125° C. and the condensate temperature was 80° to 85° C. The product was a clear, yellow liquid with fairly good solubility in mineral oil. The results are shown in Table III.

TABLE III

Additives in mineral oil ¹	Percent metallic contact ²			Coeff. of friction ³		
	240 g.	1,000 g.	4,000 g.	240 g.	1,000 g.	4,000 g.
None	85	93	99	0.103	0.093	0.085
1% triethyl borate/ethylene glycol product	0	1	11	0.029	0.055	0.066
1% triethyl borate/sorbitan mono-oleate product	0	3	70	0.087	0.079	0.082
1% triethyl borate	0	6	33	0.120	0.116	0.117

¹ Paraffinic distillate oil: Vis. Saybolt sec. 100 at 100° F; Vis. index 90-110; boiling range 650° F. to 800° F.

² Ball-on-cylinder tests, steel-on-steel (AISI 52100), 240 r.p.m., 32 minutes. The apparatus used is described in the Journal of the American Society of Lubrication Engineers, entitled "ASLE Transactions", vol. 4, pages 1-11 in 1961. "ASLE" is American Society of Lubrication Engineers. In essence, the system consists basically of a fixed metal ball loaded against a rotating cylinder. The extent of metallic contact is determined by measuring both the instantaneous and average electrical resistance between two surfaces. The apparatus is described in U.S. Patent 3,129,580 issued May 21, 1964, entitled, "Apparatus for Measuring Friction and Contacts Between Sliding Lubricating Surfaces"; inventors: Furey et al.

As can be seen from the data in Table III, the ethylene glycol derivative is quite effective in reducing metallic contact and also surprisingly potent in reducing friction by a substantial amount over the entire load range. The sorbitan monooleate derivative is much less effective and actually produces more metallic contact at the high load (4000 g.) than triethyl borate alone. The borate by itself reduces metallic contact but not friction. However, it is not nearly as effective as the borate/glycol monoester.

The two products prepared show some haze in mineral oil at 1% concentration. Trialkyl borates having a larger number of carbon atoms (e.g., from 3 to 8 carbon atoms) as the alkyl group would eliminate the haze and also produce materials of greater hydrolytic stability.

EXAMPLE 4

A. 0.1 mole tributyl phosphite (25.0 g.) and 0.1 mole C₃₆ dimer diamine (53.1 g.) was heated with stirring in flask with no solvent and in a N₂ atmosphere. Heated to 110° C. for 1 hour, the product was a clear, yellow fluid.

B. Prepared as above but heated to 200° C. for 1 hour collecting 3.9 ml. water-white fluid condensate (predominantly butanol) in the trap. The product was a clear, yellow, viscous fluid.

As seen by the data in the following Table IV, these reaction products are extremely effective in reducing metallic contact, and therefore wear, even at very high loads. Although the phosphite alone has some benefit, it is not nearly as effective as the phosphite/diamine products.

TABLE IV.—EFFECT OF PHOSPHITE/DIAMINE REACTION PRODUCTS ON METALLIC CONTACT ¹

Additives in base oil: ²	Percent metallic contact
None	100
0.5% reaction product A (tributyl phosphite/dimer diamine)	8
0.5% reaction product B (tributyl phosphite/dimer diamine)	4
0.5% tributyl phosphite	55
0.5% dimer diamine	98
1% reaction product B	1
1% tributyl phosphite	16
1% dimer diamine	92

¹ Ball-on-cylinder tests with steel-on-steel (AISI 52100) at 240 r.p.m., 4 kg. load (141,000 p.s.i. mean Hertz pressure) and 32 minutes.

² Paraffinic mineral oil having a viscosity of 35 cp. at 77° F.

EXAMPLE 5

C. 0.1 mole tetrabutyl titanate (34 g.) and 0.1 mole dimer diamine were placed in a flask and heated with stirring to 100° C. for 1 hour. The product was a clear, amber fluid.

D. Prepared as above except reaction temperature was increased to 200° C. and 1.0 ml. clear liquid (mostly butanol) collected in the trap. The product was a clear, amber fluid, slightly more viscous than C above. The results are shown in Table V.

TABLE V.—EFFECT OF TITANATE/DIAMINE MIXTURE AND REACTION PRODUCTS ON METALLIC CONTACT AND FRICTION ¹

Additives in base oil ²	Percent metallic contact	Coefficient of friction
None	99	0.115
1% molar mixture (tetrabutyl titanate/dimer diamine)	89	0.085
1% reaction product C (TBT/DD)	63	0.080
1% reaction product D (TBT/DD)	63	0.082
1% molar mixture (TBT/C ₄₀ glycol ³)	79	0.087

¹ Ball-on-cylinder tests, steel-on-steel, 1 kg. load, 240 r.p.m., 32 minutes.

² Paraffinic mineral oil having a viscosity of 35 cp. at 77° F.

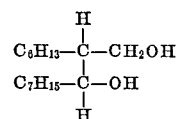
³ Glycol made by reacting 2 moles ethylene glycol with 1 mole C₃₆ dimer acid.

It can be seen that molar mixtures of tetrabutyl titanate with either C₃₆ dimer diamine or a C₄₀ glycol derived from dimer acid are effective in reducing both metallic contact and friction. In addition, the reaction products (TBT/diamine) are even more effective. (TBT alone hydrolyzes and forms insoluble material; dimer diamine alone has little effect.)

The compounds of the present invention may be used in any fluid carrier (e.g. hydrocarbons, esters, silicones, polyphenyl ethers, polyalkylene glycols, etc.) at any concentration (e.g. 0.01 to 50%, preferably 0.1 to 2) not only for lubrication (reduction of wear, scuffing, friction) but for the machining and working of metals, including titanium and its alloys, aluminum, brass and stainless steel. These compounds may also be used as lubricating fluids for non-metals (e.g. glass, plastics) and the like.

Thus the preferred lubricity additive mixtures of the present invention comprise a compound selected from the class consisting of polyols and polyamines used in a mixture with a compound selected from the class consisting of borates, silicates, phosphites and titanates. The invention is particularly concerned with a novel class of lubricity additive mixtures which are specifically adapted for use in conjunction with oleophilic liquids such as hydrocarbon lubricants and jet fuels. In accordance with the specific adaptation of the present invention, middle distillate compositions such as jet fuels are improved with respect to their lubricity by incorporating therein an effective amount of a mixture of a diol used with a compound selected from the class consisting of borates, silicates and phosphites.

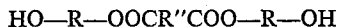
The polyols of the present invention are those which may contain from about 2 up to about 50 carbon atoms. A satisfactory glycol has 16 carbon atoms and the general formula:



wherein the C₆ and C₇ alkyl groups are branched. This material was prepared by aldolization of iso-octyl aldehyde, followed by hydrogenation. The iso-octyl aldehyde that was used, was an isomeric mixture of branched chain

aldehydes (predominantly methyl branched) prepared in the first stage of the well-known Oxo process. Here a C_7 monoolefin (prepared from butylene and propylene feed) is reacted with hydrogen and carbon monoxide under pressures of 1000 to 3000 p.s.i. and temperatures of about 300° to 400° F. in the presence of a cobalt carbonyl catalyst to form iso-octyl aldehyde.

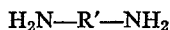
Other diols are useful for the present invention. For instance, a dihydroxy compound can be prepared by esterifying one mole of dimer acid with two moles of a glycol, thus:



wherein R is the radical of a glycol and R'' is the hydrocarbon part of the dimer acid. The diol represented by the above formula is suitable to be used with dimer acid according to the present invention. Other suitable diols are oxa alkane diols obtained for example by hydrolysis of ethylene oxide, propylene oxide or other epoxy compounds. These diols may have molecular weights between 200 and 2000. An example is 3,6,9-trioxa-1,4,7,10-tetramethyl undecane-1,11-diol.

The preferred glycols which give excellent results are those containing from about 2 to 5 carbon atoms, for example ethylene glycol and 1,4-butane diol. Specific polyhydroxic compounds that are very desirable are for example ethylene glycol.

In place of the polyols, oil-soluble polyamines may be used such as diamines having the general formula

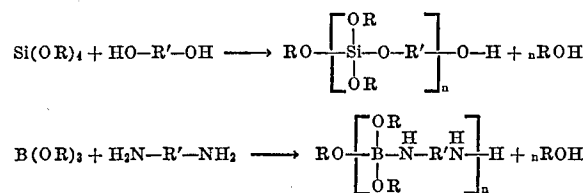


wherein R' is an alkyl radical of 10 to 40 carbon atoms, e.g. 1,12-dodecyl diamine and 1,9-heptadecyl diamine.

The oil compositions with which the preferred mixtures are used comprise a major proportion of a hydrocarbon oil and about 0.01 to 2.0%, preferably 0.1 to 1.0 weight percent of the additive mixture of the invention. However, the concentration may be considerably higher as for example up to about 30% by weight.

Although monomeric reaction products as shown above are preferred, it is to be understood that lower molecular weight polymeric products can also be used if they are soluble or dispersible enough in the carrier medium.

For example:



n is preferably equal to 1 but may equal 1, 2, 3 or 4.

What is claimed is:

1. An improved hydrocarbon composition comprising a major proportion of a middle distillate boiling in the range between about 50° and 750° F. and from about 0.01 to 1.0% by weight of an additive composition selected from the group consisting of mixtures of $P(OR)_n$ and polyamines; of $Si(OR)_n$ and polyols; of $Si(OR)_n$ and polyamines; of $B(OR)_n$ and polyols and of $Ti(OR)_n$ and polyamines and reaction products of each of said mixtures; wherein R represents a monovalent alkyl group containing from 1 to 12 carbon atoms; wherein n corresponds to the valence of the first recited element of each formula and wherein said polyamine and polyol contain between about 2 and about 50 carbon atoms.

2. The composition of claim 1 wherein said additive composition consists essentially of a mixture of alkyl phosphites and polyamines and reaction products thereof.

3. Improved hydrocarbon composition consisting essentially of a middle distillate boiling in the range from about 50° to 750° F. and containing from about 0.01 to 1.0% by weight of a mixture consisting of tetraethyl orthosilicate and C_{36} dimer tetramine.

4. Improved hydrocarbon composition consisting essentially of a middle distillate boiling in the range from about 50° to 750° F. and containing from about 0.01 to 1.0% by weight of a reaction product of tetraethyl-o-silicate and ethylene glycol.

5. Improved hydrocarbon composition consisting essentially of a middle distillate boiling in the range from about 50° to 750° F. and containing from about 0.01 to 1.0% by weight of a reaction product of triethyl borate and ethylene glycol.

6. Improved hydrocarbon composition consisting essentially of a middle distillate boiling in the range from about 50° to 750° F. and containing from about 0.01 to 1.0% by weight of a reaction product of tributyl phosphite and C_{36} dimer diamine.

7. Improved hydrocarbon composition consisting essentially of a middle distillate boiling in the range from about 50° to 750° F. and containing from about 0.01 to 1.0% by weight of a mixture of tetrabutyl titanate and C_{36} dimer diamine.

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