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LUBRICANT COMPOSITION

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This invention relates to novel lubricant compositions and a method for their use in lubricating rubbing surfaces. More particularly, the invention is concerned with the use of organo-metallic additives of tin and germanium to enhance the lubricating properties of polyester oils and greases.

The lubrication of rubbing systems which operate at extreme pressures presents unusual lubrication problems since the lubricant film between the rubbing surfaces is subjected to high shear forces. Because of these high shear forces, the lubricant films which, under low pressure operating conditions, are present upon the surfaces of the rubbing members, are forced from between the rubbing surfaces so that effective lubrication is not obtained. In order to combat these problems accompanying extreme pressure conditions, it has been the practice of the prior art to utilize lubricant additives which corrode the rubbing surfaces so as to form a film on the surfaces which, in itself, acts as a lubricant. Such additives are spoken of as E.P. additives.

A typical example of such an E.P. additive is carbon tetrachloride which breaks down in a lubrication system to form degradation products that react with the iron oxide coating on a ferrous rubbing member to form a film of ferrous chloride which acts to lubricate the rubbing metal surfaces. Since the lubrication mechanism of E.P. additives involves corrosion of the rubbing members, these additives have no lubricating effect in rubbing systems in which the rubbing members have relatively non-reactive surfaces which resist corrosion by the additive. Typical examples of such non-reactive rubbing systems are titanium-on-titanium, stainless steel-on-stainless steel, and gold-on-gold. The non-reactivity of the rubbing surfaces may be due to the resistance to corrosion of the material forming the rubbing members as is the case of gold rubbing on gold wherein the gold is essentially inert to any chemical reaction. Further, it may be due to the non-reactivity of an oxide film which is present on the surfaces of the rubbing members as in the case of a titanium-on-titanium rubbing system since titanium readily forms a surface oxide coating which is extremely nonreactive. An example of a non-metallic rubbing system in which the rubbing members are non-responsive to E.P. additives is nylon rubbing on nylon, since the nylon is substantially chemically inert. Other plastics which cannot be lubricated by E.P. lubricant additives are the polymethyl methacrylates, polyvinyl chloride and polyethylene.

It is, therefore, a general object of this invention to provide polyester lubricants, both greases and oils, with improved lubricity characteristics. A more particular object of this invention is to provide polyester lubricant compositions which are efficacious in lubricating rubbing systems operating under severe conditions in which the rubbing surfaces are non-corrodable by conventional E.P. additives. Another and more particular object is the provision of a method for utilizing improved polyester lubricants in lubricating rubbing surfaces under extreme pressure conditions. Additional objects of the invention will become apparent from the description and claims which follow.

In the accomplishment of the above objects, it has been found that the lubricity of polyester base lubricants may be greatly enhanced by adding thereto an organometallic compound of tin or germanium in a quantity sufficient to increase the lubricity of the polyester base lubricant. Although the invention is not limited to any particular mechanism of anti-wear action, it is believed that a film is formed on the rubbing surfaces, said film being formed substantially entirely from the degradation of the organometallic tin or germanium additive under the influence of heat and pressure generated at the contact points of the rubbing surfaces. Thus, the film is formed independently of any corrosive mechanism as required in the case of conventional E.P. additives and, accordingly, the film is effective in lubricating surfaces which are essentially nonreactive and have a high resistance to corrosion.

The organometallic tin or germanium additive can be present in the polyester lubricant in various concentrations and in various forms of dispersion. In the case of a polyester grease, the organometallic additive may be present in the form of well-dispersed, finely-divided particles, whereas in the case of a polyester oil, it is preferable that the organometallic additive be soluble in the oil so as to form a solution. In principle, the higher the concentration of the organometallic tin or germanium additive in the polyester lubricant, the greater is the lubricating power of the product obtained.

Experience has shown, however, that very low concentrations of the order of 0.1 percent by weight of the organotin or organogermanium additives in the polyester lubricant increases its lubricity. In view of the high cost of organotin and organogermanium compounds generally, there is an economic limit to their concentration in the base polyester lubricant, a limit which could be fixed at about 10 percent by weight in the present state of economic conditions. Moreover, when the concentration of the organotin or organogermanium additives is increased to above 10 percent, the physical properties, for example, viscosity of the resulting composition, may be quite different from those of the polyester base so that the desirable physical properties of the polyester base material may be markedly changed. In fact, with extremely high concentrations of the organotin or organogermanium additive, a situation can be reached in which the polyester lubricant is in effect the additive and the organotin or organogermanium compound is the base fluid, since the physical properties of the resulting composition are more like those of the organometallic component than like the polyester component. Thus, the preferred composition range of the invention ranges from 0.1 to 10 percent by weight of the organotin or organogermanium additive in the polyester base lubricant.

The organotin and organogermanium compounds utilized in this invention may be characterized as compounds in which there are monovalent carbon-to-metal bonds in the molecule. To be effective, these compounds must be relatively soluble in the polyester base material so as to form lubricant compositions which are stable and remain constant over extended periods of time during shipment and storage. The metal aryls such as, for example tetraphenyl tin, have not proved suitable in formulating the lubricant compositions of the invention due to the fact that they are soluble only to a very limited degree in the polyester base material. Thus, the organotin and organogermanium compounds utilized in the invention may be metal alkyls such as tetraethyl tin, dimethyldiethyl germanium, tetraeicosyl germanium, tetra-n-butyl tin and tetradecyl tin and the alicyclic-substituted metal compounds, such as tetracyclohexyl germanium and bis(2-ethylcyclopentyl) dicyclohexyl tin.

The organometallic radical bonded to the metal may be unsaturated as for example, in the case of tetra(2-propenyl) tin, tetra(1,3-butadienyl) germanium, bis(cyclohexadienyl) bis(cyclopentadienyl) tin and the like. Further included are compounds in which the metal atom is bonded to mixed hydrocarbon groups such as dicyclohexyl-dimethyl germanium, dicyclopentadienyl-diethyl tin,

bis(2,4-cyclohexadienyl) di-n-butyl germanium and the like.

The organometallic compounds used in formulating the lubricants of the invention may be halogen-substituted, may contain sulfur in the molecule and may contain various functional groups such as the carbonyl, hydroxyl and carboxyl groups. Further, the organometallic compound may contain metal-to-metal bonds as, for example, in the case of hexaethyl-digermane. Typical examples of such compounds are trimethyl germanium fluoride, triethylgermanium fluoride, trimethyltin iodide, dimethylgermanium dichloride, methylene-bis(trichlorogermane), di-n-propylgermanium oxide, bis(triethylgermyl) amine, di-n-butyltin sulfide, triethyltin hydroxide, bis(triethyltin) acetylene and diethylgermanium imine.

Since the solubility of the organometallic tin or germanium compounds in diester oils and greases generally decreases as the number of carbon atoms per molecule is increased, a preferred class of organometallic compounds for use as diester additives is represented by the non-aromatic organometallic compounds of tin and germanium wherein each molecule contains from 2 to 36 carbon atoms. It has been found that the compounds within this range are soluble in diester oils to the extent required to form an effective lubricant film on the surface of the rubbing members during use of the lubricant. At the same time, because of the solubility of the preferred organometallic compounds in diester oils, the concentration of the organometallic compound is uniform throughout the lubricant and forms a stable composition which remains constant over extended periods of time during shipment and storage. Compounds having branched chain hydrocarbon constituent groups are generally more unstable than are their straight chain counterparts and thus, straight chain substitution is generally found to produce a better diester lubricant additive.

Methods for the preparation of the organometallic tin and germanium compounds used in formulating the lubricant compositions of the invention are set forth in "Die Chemie der metallorganischen Verbindungen" by Drs. Krause and von Grosse. The book was produced in the form of a Photo-Lithoprint Reproduction by Edwards Brothers, Inc., of Ann Arbor, Michigan, in 1943 under the authority of the Alien Property Custodian, License No. A–245.

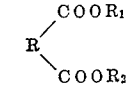
The polyester lubricant base materials used in formulating the lubricant compositions of my invention may be either oils or greases. The oils may be formed by the reaction of a polycarboxylic acid with a mono-hydric alcohol, the reaction of a polyhydric alcohol with a mono-carboxylic acid, reaction between a polyhydric alcohol and a polycarboxylic acid, or combinations of the above reactions, such as, for example, reaction of a dicarboxylic acid with a glycol and a mono-hydric alcohol, reaction of a glycol with a dicarboxylic acid and a mono-carboxylic acid, or the reaction of a glycol, a mono-hydric alcohol, a dicarboxylic acid and a mono-carboxylic acid. The acids may be mono-carboxylic aliphatic acids such as, for example, propionic acid, valeric acid, 2-ethyl enanthic acid, 2,2-di-propyl butyric acid or 3-(2-methylhexyl) valeric acid. They may contain unsaturated linkages, such as, for example, in senecioic acid, sorbic acid, or angelic acid; they may be polycarboxylic aliphatic acids such as succinic acid, glutaric acid, azelaic acid, 5-octene-1,8-dicarboxylic acid, or 3-hexene-2,3,4-tricarboxylic acid, and they may be aromatic or cycloaliphatic acids, such as cyclohexaneacetic acid, 1,4-cyclopentylenebis acetic acid, phthalic acid, hemimellitic acid, and terephthalic acid.

The alcohols used in preparing the polyester lubricant base materials may be aliphatic mono-hydric alcohols such as propanol, 2-ethyl-3-hexenol, 2-ethyl-4-propyl heptanol, 2-butenol, or 2-methyl propanol. They may be polyhydric aliphatic alcohols, such as, 1,6-hexamethylene glycol, 1,10-decamethylene glycol, 2-hexene-1,6-diol, and

1,6-heptylene glycol, and they may be mono or polyhydric alicyclic or aromatic alcohols, such as 4-[m-(2-hydroxyethyl) phenyl] butanol, 3-(2-hydroxyethyl) cyclohexanebutanol, p-(hydroxymethyl) phenethyl alcohol, α-methyl-p.xylene-α,α′-diol, 1,4 - cyclohexane-β,β′-diethyl-dimethanol, 2,3-bis(4-hydroxybutyl) benzyl alcohol, 4,4′-[3-(3-hydroxyhexyl)-o-phenylene] dibutanol, and 5-[3-(3-hydroxypropyl) cyclopenta-2,4-dienylene] 3-ethyl amyl alcohol.

The polyester base greases used in formulating lubricant compositions of the invention are formed by admixing a soap with a diester oil. Such soaps may be derived from animal or vegetable fats or fatty acids, wool grease; rosin, or petroleum acids. Typical examples of such soaps are lead oleate, lithium stearate, aluminum tristearate, calcium glycerides, sodium oleate and the like. In addition, the diester greases may contain unreacted fat, fatty acids, and aikali; unsaponifiable matter including glycerol and fatty alcohols; rosin or wool grease; water; and certain additives which may function as modifiers or peptizers.

When taken in their broadest sense, the lubricant compositions of my invention include the addition of an organometallic compound of tin or germanium, as described hereinbefore, to any known polyester lubricant material. More specifically, however, I have found that lubricant compositions comprising an organometallic compound of tin or germanium admixed with a diester, as set forth in the following generic formula, provide superior lubricant compositions and it is these lubricant compositions which are particularly preferred within the scope of my invention. The diester lubricant materials used in formulating the preferred lubricant compositions have the following generic formula:



where R is divalent aliphatic hydrocarbon radical which may be saturated or unsaturated and has from 2 to 8 carbon atoms and R_1 and R_2 are branched chain alkyl groups having at least 4 carbon atoms.

As shown by the above generic formula, the diesters utilized in formulating the preferred lubricant compositions, including esters of succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acid. Typical examples of such esters are diisooctyl azelate, di(2-ethylhexyl) sebacate, di-sec-amyl sebacate, diisooctyl adipate, di(2-ethylhexyl) adipate, di(2-ethylhexyl) azelate, di(1-methyl-4-ethyloctyl) glutarate, di-isoamyl adipate, di(2-ethylhexyl) glutarate, di(2-ethylbutyl) adipate, di-tetradecyl sebacate and di(2-ethylhexyl) pinate.

The preferred diesters are prepared by esterifying one mole of a dicarboxylic acid having the general formula: $HOOC(CH_2)_xCOOH$, where x is an integer of from 2 to 8, with 2 moles of a branched chain alcohol containing at least 4 carbon atoms. Typical of the reactions embraced herein are the reactions of succinic, glutaric, adipic, pimelic, suberic or azelaic acid with sec-amyl alcohol, 3-methyl butanol, 2 ethyl hexanol or the branched chain secondary alcohols undecanol or tetradecanol.

The preferred diester lubricant fluids have molecular weights ranging from about 300 to about 600 and freezing and pouring points from about −40° to less than about −100° F. The flash and fire points range from about 300° F. to about 500° F. and their spontaneous ignition temperatures range from about 100° to about 800° F. The diesters made by reacting a dicarboxylic acid with a branched chain alcohol have been found to have superior viscometric properties as compared with diesters made by reacting dihydric alcohols with monocarboxylic acids, and thus, diesters prepared by the former method are preferred in formulating the lubricant compositions of my invention.

In formulating the polyester grease compositions within the scope of my invention, I have found that the greases prepared by admixing a lithium soap with the polyester oils have superior oxidative stability as compared with greases formulated with other soaps, such as, for example, the sodium, calcium or lead soaps. Thus, the polyester greases employing a lithium soap constitute a preferred embodiment of lubricant compositions within the scope of my invention.

In order to further illustrate the lubricant compositions of my invention, there are set forth the following examples showing typical lubricant compositions within the scope of the present invention. Unless otherwise specified, proportions given in these examples are on a weight basis.

Example I

One part of tetramethyltin is blended with 99 parts of diisooctyl adipate having a viscosity of 35.4 SUS at 210° F., a viscosity of 57.3 SUS at 100° F., a viscosity of 3,980 SUS at −40° F. and a viscosity of 22,500 at −65° F. Its viscosity index is 143, its ASTM pour point is below −80° F. and its specific gravity (60° F./60° F.) is 0.926.

Example II

Five parts of di-n-propylgermanium oxide are blended with di(1-methyl-4-ethyloctyl) glutarate. Di(1-methyl-4-ethyloctyl) glutarate has a freezing point of −80° F., a specific gravity, d_4^{25} of 0.901, a kinematic viscosity of 3.45 centistokes at 210° F., 15.9 centistokes at 100° F., 485 centistokes at 0° F. and 7,430 centistokes at −40° F.

Example III

Eight parts of tetraeicosylgarmanium are blended with 92 parts of grease comprising 12 percent of lithium stearate, 1 percent of polybutene (12,000 molecular weight), 0.2 percent of 4-tert-butyl-2-phenyl phenol, 2 percent of calcium xylyl stearate, 33.8 percent of di(2-ethylhexyl) sebacate and 51 percent of di(2-ethylhexyl) adipate.

Example IV

To 99.9 parts of diethylphthalate is added 0.1 part of tetradodecyltin. Diethylphthalate has a freezing point of −27° F. and a specific gravity, d_4^{25}, of 1.114. Its viscosity at 210° F. is 1.73 centistokes, at 100° F. is 6.26 centistokes and at 0° F. is 121 centistokes.

Lubricant compositions similar to that of Example IV are prepared by adding 0.1 part of tetradodecyltin to 99.9 parts of one of the following diester fluids: bis(2-ethylhexyl) terephthalate, 2-butylhexyl 3-(2-butylhexyloxycarbonyl) - 2,4 - cyclopentadienepropionate, tris(2-ethylpentyl)trimesate, 2,11-diethyldodecamethylene 1,4-cyclohexane-diacetate, 2,14-dipropylpentadecamethylene terephthalate, 1,3-cyclopentylenebis(3 - ethylhexamethylene) terephthalate, and 2,16-diethylheptadecamethylene pimelate.

Example V

Five parts of tetraethylgermanium are blended with 95 parts of diisooctyl azelate having a kinematic viscosity of 3.34 centistokes at 210° F., 7000 centistokes at −65° F. (ASTM 445–52T), an ASTM slope from −40° F. to 210° F. of 0.693 (ASTM D341–43) and a pour point of −85° F. (ASTM D97–47). Its flash point is 425° F. (ASTM D92–52), and is specific gravity is 0.9123 at 25° C.

Example VI

To 97 parts of diisoamyl adipate is added 3 parts of dimethyltin sulfide. Diisoamyl adipate has a viscosity of 1.71 centistokes at 210° F., 4.93 centistokes at 100° F., 180 centistokes at −40° F. and 840 centistokes at −65° F. Its viscosity index is 125, its ASTM pour point is below −80° F. and its specific gravity (60° F./60° F.) is 0.938.

Example VII

Seven parts of dimethylgermanium dihydroxide are blended with 93 parts of di-sec-amyl sebacate. Di-sec-amyl sebacate has a viscosity of 34.2 Saybolt Universal seconds (SUS) at 210° F., a viscosity of 51.7 SUS at 100° F., a viscosity of 2,660 SUS at −40° F. and a viscosity of 15,100 SUS at −65° F. Its viscosity index is 130, its pour point is below −80° F. and its specific gravity (60° F./60° F.) is 0.915.

Example VIII

Nine parts of tetranonylgermanium are blended with 91 parts of di(2-ethylhexyl) glutarate. Di(2-ethylhexyl) glutarate has a freezing point of −80° F., a specific gravity, d_4^{25}, of 0.922, a viscosity of 2.17 centistokes at 210° F., a viscosity of 7.40 centistokes at 100° F., a viscosity of 94.7 centistokes at 0° F. and a viscosity of 715 centistokes at −40° F. Its kinematic viscosity index is 106 and its ASTM slope from −40° F. to 210° F. is 0.80.

Example IX

Three parts of di-n-butyltin sulfide are blended and mixed with 97 parts of a grease comprising 12.5 percent of lithium stearate, 1 part of polybutene (12,000 molecular weight), 0.2 percent of 4-tert-butyl-2-phenyl phenol, 2 percent of calcium xylyl stearate and 84.3 percent of di(2-ethylhexyl) sebacate.

Example X

Four parts of bis-triethylgermanium sulfide are blended with 96 parts of di(2-ethylhexyl) sebacate having a viscosity of 37.4 SUS at 210° F., 68.9 SUS at 100° F., 6,410 SUS at −40° F. and 35,800 SUS at −65° F. Its viscosity index is 154, its ASTM pour point is below −80° F. and its specific gravity (60° F./60° F.) is 0.912.

Example XI

To 99 parts of di(2-ethylbutyl) adipate is added 1 part of triethylgermanium bromide. Di(2-ethylbutyl) adipate has a freezing point of −15° F., a specific gravity, d_4^{25}, of 0.934, a viscosity of 1.89 centistokes at 210° F., a viscosity of 5.68 centistokes at 100° F., a viscosity of 51 centistokes at 0° F. and a kinematic viscosity index of 123.

Example XII

Ten parts of bis(triethylgermanium) amine are mixed with 90 parts of a grease comprising 11 percent of lithium stearate, 0.4 percent of 4-tert-butyl-2-phenyl phenol, 1 percent of polybutene (12,000 molecular weight), 1 percent of sorbitan monooleate and 86.6 percent of di [1-(2-methylpropyl)-4-ethyloctyl] sebacate.

Example XIII

Seven parts of di-n-butyltin dilaurate are blended with 93 parts of 1,6-hexamethylene glycol di(2-ethylhexanoate). 1,6-hexamethylene glycol di(2-ethylhexanoate) has a specific gravity, d_4^{25}, of 0.908, a viscosity of 2.35 centistokes at 210° F., a viscosity of 8.64 centistokes at 100° F., a viscosity of 129 centistokes at 0° F. and a viscosity of 1,090 centistokes at −40° F. Its kinematic viscosity index is 96 and its ASTM slope from −40° F. to 210° F. is 0.79.

Example XIV

Two parts of dicyclohexyl-diethyl tin are blended with 98 parts of di(2-ethylhexyl) azelate having a kinematic viscosity of 2.96 centistokes at 210° F., 11 centistokes at 100° F., 1,150 centistokes at −40° F., and 6,400 centistokes at −65° F. as measured by the test set forth in ASTM 445–42T. Its ASTM slope from −40° F. to 210° F. is 0.724 (ASTM D341–43), its pour point is −100° F. (ASTM D97–47), its flash point is 420° F. (ASTM D92–52) and its specific gravity, as measured at 25° C., is 0.9124.

Example XV

Four parts of tetra-allyltin are blended and mixed with 96 parts of a grease comprising 12 percent of lithium stearate, 2.5 percent of polybutene (12,000 molecular weight), 0.2 percent of 4-tert-butyl-2-phenyl phenol and 85.3 percent of di(2-ethylhexyl) adipate.

Example XVI

Six parts of hexaethyl digermane are blended and mixed with 94 parts of a grease consisting of 12 percent of lithium stearate and 88 percent of di(2-ethylhexyl) sebacate.

Other lubricant compositions similar to the lubricant of Example XVI are prepared by mixing 6 parts of hexaethyl digermane with grease compositions comprising 88 percent of di(2-ethylhexyl) sebacate admixed respectively with calcium stearate, lead naphthenate, barium oleate, strontium stearate and magnesium stearate.

Numerous lubricant compositions containing a polyester oil or grease and an organometallic compound as defined above were tested in a four-ball wear machine to determine the lubricity of the respective lubricant compositions relative to operation with non-additive polyester oils or greases. The four-ball wear machine is described by Larsen and Perry in the "Transactions of the A.S.M.E.," January 1945, pp. 45–50.

The four-ball wear machine utilizes four balls of equal size arranged in a tetrahedral formation. The bottom three balls are held in a non-rotatable fixture which is essentially a universal chuck that holds the balls in abutting relation to each other. Since the bottom three balls are of equal size, their centers form the apices of an equilateral triangle. The top ball is affixed to a rotatable spindle whose axis is positioned perpendicularly to the plane of the ball holder and in line with the center point of the triangle whose apices are the centers of the three bottom stationary balls.

In operation, the four balls are immersed in the lubricant composition to be tested and the fixture holding the three bottom balls is moved upwardly so as to bring the three fixed lower balls into engagement with the upper rotating ball. To increase the load, the fixture is moved upwardly and axially of the rotating spindle affixed to the upper ball.

The lubricity of the lubricant under test is determined by the amount of wear occurring on the lower balls at the points of contact with the upper rotating ball. If the lubricant is completely effective, the amount of wear will be negligible. On the other hand, if the lubricant is not completely effective under the test conditions, the upper ball may weld or seize to the lower balls due to the heat of friction at the contact points, or the wear which occurs will be excessive. If seizure does not occur, the average diameter of the circular scar areas of the lower balls is measured so as to give a quantitative basis for comparing the test results with those of other tests. As the severity of the test conditions is increased with a given lubricant composition, the likelihood of excessive wear of the lower balls is increased.

To illustrate the effectiveness of the lubricant compositions of my invention, the following examples are set forth which show the superiority of my lubricant compositions when they are tested in a four-ball wear machine.

Example XVII

Non-additive-containing di(2-ethylhexyl) sebacate was run in the four-ball wear machine under the following test conditions: the speed of rotation of the upper ball was 572 r.p.m., the test temperature was 50° C., and the balls were ½ inch in diameter and constructed of SAE 52–100 steel. The machine was run for two hours under the above conditions at a loading of 1 kilogram, after which the balls were disassembled and the average scar diameter on the lower three balls was measured and found to be 0.15 millimeter.

Example XVIII

Non-additive-containing di(2-ethylhexyl) sebacate was run in the four-ball wear machine for two hours at a loading of 2.5 kilograms under the test conditions utilized in Example XVII. The average scar diameter on the lower three balls was 0.30 millimeter.

Example XIX

Non-additive-containing di(2-ethylhexyl) sebacate was run in the four-ball wear machine under the test conditions utilized in Examples XVII and XVIII for a period of two hours at a loading of 10 kilograms. The average scar diameter on the lower three balls was 0.53 millimeter.

Example XX

A lubricant composition comprising 5 parts by weight of di-n-butyltin sulfide admixed with 95 parts of di(2-ethylhexyl) sebacate was run in the four-ball wear machine under the identical test conditions utilized in Example XVII, namely, a two hour run at a 1 kilogram loading. The average scar diameter on the lower three balls was measured and found to be 0.11 millimeter.

Example XXI

The lubricant composition used in Example XX was run in the four-ball wear machine under the identical test conditions utilized in Example XVIII. The average scar diameter on the lower three balls was 0.14 millimeter.

Example XXII

The lubricant composition utilized in Example XX was run in the four-ball wear machine under the identical test conditions utilized in Example XIX, namely, a two hour run at a 10 kilogram loading. The average scar diameter on the lower three balls was 0.26 millimeter.

The comparison of the test results set forth in Examples XVII through XXII clearly demonstrates the superiority of the lubricant composition of the invention over the non-additive-containing di(2-ethylhexyl) sebacate. The lubricant composition of the invention was more effective than the base lubricant at loads of 1, 2.5 and 10 kilograms with the effectiveness being more marked as the load was increased. Thus, the average scar diameter obtained in the 2.5 and 10 kilogram loading was approximately one half that obtained when utilizing the non-additive-containing lubricant material under the same test conditions.

Further tests are conducted in the four-ball wear machine as follows:

Example XXIII

Two lubricant compositions, one being di(2-ethylhexyl) glutarate and the other being the lubricant composition of Example VIII are tested in the four-ball wear machine under the following conditions:

The upper ball rotating at a speed of 572 r.p.m., the ambient temperature being 50° C. and the balls being ½ inch in diameter and constructed of SAE 52–100 steel. When the respective lubricant compositions are subjected to identical loadings for identical times in the four-ball wear machine under the above conditions, the lubricant composition of the invention, namely the composition of Example VIII is far superior to the non-additive-containing diisooctyl azelate.

Example XXIV

Two lubricant compositions, one being grease comprising 11 percent of lithium stearate, 1 percent of polybutene (12,000 molecular weight), 0.4 percent of 4-tert-butyl-2-phenyl-phenol, 1 percent of sorbitan mono-oleate, and 86.6 percent of di[1-(2-methyl propyl)-4-ethyloctyl] sebacate, and the other being a lubricant blend comprising 10 parts of bis(triethylgermanium)amine with 90 parts of the aforementioned grease, are tested in the four-ball wear machine under the conditions set forth in Example XXIII. When so tested under conditions of identical loading and

for identical times, the lubricant composition of the invention, namely that set forth in Example XII, will prove far superior to the non-organometallic-containing polyester grease composition.

Example XXV

When tested in the four-ball wear machine under the conditions of Examples XXIII and XXIV, a lubricant composition of the invention comprising 5 parts of tetraethyl germanium blended with 95 parts of diisooctyl azelate provides superior lubrication as compared with the lubrication provided by non-additive-containing diisooctyl azelate.

Example XXVI

A non-additive-containing diester lubricant comprising solely diisoamyl adipate was run in the four-ball wear machine under the following test conditions: the speed of rotation of the upper ball was 572 r.p.m., the testing temperature was 50° C., and the balls were ½ inch in diameter and constructed of SAE 52–100 steel. Following a two hour run at a load of 20 kilograms, the balls were disassembled and the average scar diameter on the lower three balls was 0.95 millimeter.

Example XXVII

A lubricant composition comprising 10 parts by weight of di-n-butyltin dilaurate admixed with 90 parts of diisoamyl adipate was run in the four-ball wear machine for two hours at a loading of 20 kilograms under the same test conditions utilized in Example XXVI. The average scar diameter on the lower three balls was measured and found to be 0.72 millimeter.

Example XXVIII

Non-additive-containing di-tridecyl azelate was tested in the four-ball wear machine under the same general conditions utilized in Examples XXVI and XXVII. The loading applied was 40 kilograms for a period of two hours after which the balls were disassembled and the average scar diameter on the lower three balls was measured and found to be 0.62 millimeter.

Example XXIX

A lubricant composition comprising 5 parts by weight of di-n-butyltin sulfide admixed with 95 parts of di-tridecyl azelate was tested under the identical conditions utilized in Example XXVIII, namely, a 40 kilogram loading applied for 2 hours. The average scar diameter on the lower three balls was 0.39 millimeter.

The results set forth in Example XXIII through XXIX clearly demonstrate superiority of my lubricant compositions as compared with non-additive-containing diester lubricant materials. The scar diameter obtained in Example XXVII was reduced to approximately 76 percent of the scar diameter obtained in Example XXVI, utilizing the same base diester material under identical test conditions. The scar diameter obtained in Example XXIX is approximately 63 percent of that obtained in Example XXVIII utilizing the same base diester lubricant material under identical test conditions. This is an even more striking improvement than is afforded by the comparison between Examples XXVI and XXVII. The results in Examples XXIII through XXIX illustrate the effectiveness of my lubricant compositions over a wide range of organotin and organogermanium compounds admixed with a wide range of diester lubricant materials at loads up to 40 kilograms, so as to obtain effective lubrication in a manner heretofore unknown in the lubrication art.

Further wear testing of the lubricant compositions of the invention was done in the four-ball wear machine utilizing rubbing surfaces other than steel. The following examples illustrate the results obtained from these tests.

Example XXX

A non-additive lubricant composition comprising 50 parts by weight of di(2-ethylhexyl) sebacate, blended with 50 parts of diisoamyl adipate was tested in the four-ball wear machine under the following conditions: the speed of rotation of the upper ball was 572 r.p.m., the test temperature was 50° C., the three stationary bottom balls were ½ inch in diameter and constructed of brass, and the upper ball was ½ inch in diameter and constructed of SAE 52–100 steel. The lubricant was tested for one hour under the above conditions at a 10 kilogram loading, whereupon the balls were disassembled and the average scar diameter on the bottom three brass balls was found to be 0.85 millimeter.

Example XXXI

A lubricant composition comprising 7 parts by weight of tri-n-butyltin chloride admixed with 90 parts of the diester lubricant utilized in Example XXX, was tested in the four-ball wear machine under the identical conditions utilized in Example XXX. Following the test, which comprised a 10 kilogram loading for a period of one hour, the average scar diameter on the stationary brass balls was found to be 0.55 millimeter.

Example XXXII

Non-additive-containing di(2-ethylhexyl) sebacate was tested in the four-ball wear machine under the following conditions: the speed of rotation of the upper ball was 79 r.p.m., the test temperature was 50° C., the balls were ½ inch in diameter, constructed of hard steel and having a 0.001 inch thickness of gold plating thereon. Two runs were conducted under a 0.5 loading at the above conditions. Seizure occurred at the end of 18 minutes in the first run and after 11½ minutes in the second run, and was manifested in each case by rapid extensive tearing of the gold plate on the balls and the formation of large particles of debris.

Example XXXIII

A lubricant composition comprising 5 parts by weight of di-n-butyltin sulfide admixed with 95 parts of di(2-ethylhexyl) sebacate was tested in the four-ball wear machine under the identical conditions used in Example XXXIII. Effective lubrication was achieved for a period of two hours at the 0.5 kilogram loading.

The results of Examples XXX through XXXIII further demonstrate the increased lubricating effectiveness of the lubricant compositions of the invention as compared with non-additive-containing diester materials. Comparison of the results obtained in Examples XXX and XXXI shows a reduction in scar diameter, achieved through the additive use of 7 parts of tri-n-butyltin chloride, to 64.5 percent of that obtained when utilizing a 50–50 non-additive-containing mixture of di(2-ethylhexyl) sebacate and diisoamyl adipate. The results of Examples XXXII and XXXIII even more strikingly illustrate the effectiveness of my lubricant compositions. In Example XXXIII, utilizing a composition of the invention, effective lubrication was obtained for two hours, whereas, with the non-additive-containing lubricant composition of Example XXXII the average time to seizure was 14.7 minutes. In terms of the time of effective lubrication, Example XXXIII represents an increase in lubricating effectiveness of approximately 8 times that obtained in Example XXXII.

As shown by the preceding examples, the lubricity of polyester lubricant compositions are greatly increased by the addition thereto of organometallic compounds of tin or germanium. This enables the utilization of polyester base lubricants in applications heretofore found impossible such as, for example, utilization under extreme pressure conditions in the lubrication of rubbing surfaces which are relatively inert.

The lubricating effectiveness of the lubricant composi-

tions of my invention may be greatly increased by proper "running-in" of the lubricant composition between the rubbing surfaces to be lubricated. The "running-in" comprises subjecting the rubbing surfaces when in contact with the lubricant composition of the invention to a loading that is initially low, being well below the operating load. This load is maintained for a time sufficient to build up a film on the rubbing surfaces that is formed from the degradation of the organometallic additive component in the lubricant. Subsequently the load is increased up to the operating load. Variations of this procedure may involve: (1) Gradually increasing the load during the period of film formation; that is to say, the initially low loading is gradually increased at such rate that the build-up of a degradation film on the rubbing surfaces is substantially complete before the operating load is attained and (2) utilizing a constant loading during the period of film formation, which load is not increased until the build-up of a degradation film from the organometallic additive on the rubbing surfaces is substantially complete.

Although the lubricating mechanism which takes place when utilizing a lubricant of my invention, is not precisely understood, it is believed that it involves a film formation on the rubbing surfaces due to degradation of the organometallic tin or germanium component in the lubricant. Inasmuch as this film formation requires time and is not an instantaneous phenomenon, the mechanism is not effective when the lubricating surfaces are subjected to an initially high loading, since the loading causes failure before a film can be formed on the rubbing surfaces. The aforementioned method takes cognizance of this fact by allowing sufficient time for build-up of the degradation film on the rubbing surfaces before the application of high loads to the rubbing system. In this manner, the lubricant compositions of my invention are utilized to their full effectiveness so as to enable the utilization of polyester base lubricants in a manner heretofore found impossible.

The beneficial effects of my method are illustrated by way of the following examples:

Example XXXIV

When the lubricant composition set forth in Example VI is run in the four-ball wear machine under the following test conditions in which the speed of rotation of the upper ball is 79 r.p.m., the ambient temperature is 50° C., the 4 balls are ½ inch in diameter, constructed of 52–100 steel and having a 0.001 inch coating of pure gold, the following results are obtained. The lubricant composition is subjected in one test run to an initial loading of 10 kilograms, whereas, in a second test run, the lubricant composition is run for 120 minutes at a load of 1 kilogram, after which loads of 2.5, 10, 20 and 30 kilograms are applied for 2½ minute intervals respectively. When so tested, the lubricant composition is effective in providing lubrication during the second test run at loads above those at which failure occurs in the first test run.

Example XXXV

The lubricant composition of Example XII is tested in the four-ball wear machine under the conditions of Example XXXIV, and is found effective under the conditions of the second test run at loads in excess of the loading which in the first test run will cause failure.

Example XXXVI

The lubricant composition of Example VIII is tested under the same conditions as in Examples XXXIV and XXXV, and provides effective lubrication when utilized with a "running-in" period, as in the second test run, at loads in excess of the high initial loads which cause almost instantaneous failure in the first test run.

The method illustrated in Examples XXXIV through XXXVI finds application when utilizing any of the lubricant compositions of my invention. Thus, it will be found that the lubricating effectiveness of, for example, the lubricant composition of Example II comprising 5 parts of di-n-propyl germanium oxide in 95 parts of di(1-methyl-4-ethyloctyl) glutarate, the lubricant composition of Example I comprising one part of tetramethyltin in 99 parts of diisooctyl adipate, the composition of Example IX comprising 3 parts of di-n-butyltin sulfide mixed with 97 parts of a grease comprising 12.5 percent of lithium stearate, 1 part of polybutene (12,000 molecular weight), 0.2 percent of 4-tert-butyl-2-phenyl phenol, 2 percent of calcium xylyl stearate and 84.3 percent of di(2-ethylhexyl) sebacate, or the composition of Example X comprising 4 parts of bis-triethylgermanium sulfide in 96 parts of di(2-ethylhexyl) sebacate are greatly improved when utilized according to the method heretofore set forth.

The many examples set forth in the preceding portions of this specification are by way of illustration only and should not be construed as in any way limiting the scope of my invention. Obvious variations within the scope of the invention will be readily apparent to one skilled in the art such as for example, using a plurality of organometallic compounds of tin or germanium as additives to a single polyester base lubricant, or in varying the time, load and lubricant composition from those set forth in Examples XXXIV through XXXVI. Other variations within the scope of my invention include the utilization of polyester lubricant materials, other than those set forth in the preceding examples, in formulating my lubricant compositions. Such polyester lubricant materials would include esters of polycarboxy-substituted-heterocyclic-ring compounds, polyhydric-substituted-heterocyclic-ring compounds and aliphatic polyhydric and polycarboxy compounds containing elements such as sulfur and nitrogen in their structure.

Further, the polyester base lubricant material may consist of a complex mixture of various esters, such as, for example, a mixture of an azelate with a glycol ester or a diester derived from a polycarboxylic acid other than azelaic acid, or a mixture of a complex polyester with such components as mono-esters or diesters, ether esters, glycols, polyglycols, glycol ethers, formals, polyformals, or blends of two or more of such components, and may include a polysiloxane admixed therewith.

The lubricant compositions of my invention may also contain other compounds, such as soaps, antioxidants, thickeners, and antifoaming agent additives which are present in commercial polyester lubricants, since such additives in no way inhibit the effectiveness of the lubricant compositions of the invention. The lubricant compositions of my invention are not restricted to use with any particular rubbing system, metal or non-metal, since their mechanism of operation is effective in lubricating any combination of rubbing surfaces. Their greatest utility, however, is found in lubricating chemically inactive rubbing surfaces since it is in this area that conventional E.P. additives are ineffective.

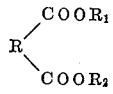
A further utility of the lubricant compositions of the invention is in lubricating electrically conductive noble metal rubbing systems, such as, for example, the silver-silver of silver-graphite contacts found in electrical switches, relays, motors and electrical generating equipment. The lubricant films laid down by many of the lubricant compositions of the invention have high electrical conductivity and, therefore, would not inhibit the transfer of electrical current between the rubbing members.

Having set forth and described the invention fully by way of the preceding examples and explanation, I deside to be limited only by the scope of the following claims which define my invention.

I claim:

1. A composition of matter adapted for lubricating rub-

bing surfaces, which composition consists essentially of a diester base lubricant having the formula

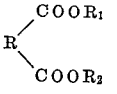


where R contains from two to eight carbon atoms and is a divalent aliphatic hydrocarbon radical selected from the group consisting of saturated and unsaturated radicals, and R_1 and R_2 are branched chain alkyl groups containing from four to about 14 carbon atoms, said diester having admixed therewith from about 0.1 to about 10 percent of a compound selected from the class consisting of tetraalkyltin compounds and tetraalkylgermanium compounds.

2. The lubricating composition of claim 1 wherein said compound is tetraethylgermanium.

3. The lubricating composition of claim 1 wherein said compound is tetramethyltin.

4. A method for lubricating rubbing surfaces with a lubricant consisting essentially of a diester base lubricant having the formula



where R contains from two to eight carbon atoms and is a divalent aliphatic hydrocarbon radical selected from the group consisting of saturated and unsaturated radicals and R_1 and R_2 are branched chain alkyl groups containing from four to about 14 carbon atoms, said diester having admixed therewith from about 0.1 to about 10 percent of a compound selected from the class consisting of tetraalkyltin compounds and tetraalkylgermanium compounds, which method comprises rubbing the surfaces together in the presence of said lubricant at a load which is below the operating load until a film is formed on the rubbing surfaces from the degradation of said compound, and thereafter increasing the load up to the operating load.

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