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3,203,896

LUBRICATING COMPOSITION

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This invention relates to an improved lubricating composition and, more particularly, to a lubricating composition containing a particular additive mixture which serves to maintain the lubricity properties of the composition during use.

The advancing technology in the mechanical field is accompanied by the need for improved operation of moving metal parts. As this technology advances, the moving parts are required to operate satisfactorily under more severe conditions including higher speeds, higher temperatures, greater loads, longer periods of use, etc. In aircraft, this increased severity also includes operation at higher altitudes. Moving parts inherently require lubrication and the advancing technology in the mechanical field of necessity requires correspondingly improved lubricants. Great strides have been made in the art of lubrication as, for example, the more careful selection of the fraction and types of mineral oil used for lubrication, improved refining and treating of the mineral oils, development and use of synthetic lubricating oils, etc.

Even with the improved lubricating oils presently available, there is a constant need to further improve such oils. As these oils are further improved, the severity of the operation of the moving parts can be correspondingly increased, with the resultant improved efficiency of operation. One method of improving the properties of lubricating oils is by the incorporation of additives therein. The present invention is directed to the use of a novel additive to improve the properties of lubricating oils.

The present invention is used with any lubricating oil, which may be of natural or synthetic origin. The mineral oils include those of petroleum origin and are referred to as motor lubricating oil, railroad type lubricating oil, marine oil, transformer oil, turbine oil, differential oil, diesel lubricating oil, gear oil, cylinder oil, specialty products oil, etc. Other natural oils include those of animal, marine or vegetable origin.

Synthetic lubricating oils are of varied types including aliphatic esters, polyalkylene oxides, silicones, esters of phosphoric and silicic acids, highly fluorine-substituted hydrocarbons, etc. Of the aliphatic esters, di-(2-ethylhexyl) sebacate is being used on a comparatively large commercial scale. Other aliphatic esters include dialkyl azelates, dialkyl suberates, dialkyl pimelates, dialkyl adipates, dialkyl glutarates, etc. Specific examples of these esters include dihexyl azelate, di-(2-ethylhexyl) azelate, di-3,5,5-trimethylhexyl glutarate, di-3,5,5-trimethylpentyl glutarate, di-(2-ethylhexyl) pimelate, di-(2-ethylhexyl) adipate, triamyl tricarallylate, pentaerythritol tetracaproate, dipropylene glycol dipelargonate, 1,5-pentanediol-di-(2-ethylhexanonate), etc. The polyalkylene oxides include polyisopropylene oxide, polyisopropylene oxide diether, polyisopropylene oxide diester, etc. The silicones include methyl silicone, methylphenyl silicone, etc., and the silicates include, for example, tetra-

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isooctyl silicate, etc. The highly fluorinated hydrocarbons include fluorinated oil, perfluorohydrocarbons, etc.

Additional synthetic lubricating oils include (1) neopentyl glycol esters, in which the ester group contains from 3 to 12 carbon atoms or more, and particularly neopentyl glycol propionates, neopentyl glycol butyrates, neopentyl glycol caproates, neopentyl glycol caprylates, neopentyl glycol pelargonates, etc., (2) trimethylol alkanes such as trimethylol ethane, trimethylol propane, trimethylol butane, trimethylol pentane, trimethylol hexane, trimethylol undecane, trimethylol dodecane, etc., as well as the esters thereof and particularly triesters in which the ester portions each contain from 3 to 12 carbon atoms and may be selected from those hereinbefore specifically set forth in connection with the discussion of the neopentyl glycol esters, and (3) tricresylphosphate, trioctylphosphate, trinonylphosphate, tridecylphosphate, as well as mixed aryl and alkyl phosphates, etc.

The present invention also is used in the stabilization of greases made by compositing one or more thickening agents with an oil of natural or synthetic origin. Metal base synthetic greases are further classified as lithium grease, sodium grease, calcium grease, barium grease, strontium grease, aluminum grease, etc. These greases are solid or semi-solid gels and, in general, are prepared by the addition to the lubricating oil of hydrocarbon soluble metal soaps or salts of higher fatty acids as, for example, lithium stearate, calcium stearate, aluminum naphthenate, etc. The grease may contain one or more thickening agents such as silica, carbon black, talc, organic modified bentonite, etc., polyacrylates, amides, polyamides, aryl ureas, methyl N-n-octadecyl terephthalomate, etc. Another type of grease is prepared from oxidized petroleum wax, to which the saponifiable base is combined with the proper amount of the desired saponifying agent, and the resultant mixture is processed to produce a grease. Other types of greases in which the features of the present invention are usable include petroleum grease, whale grease, wool grease, etc., and those made from inedible fats, tallow, butcher's waste, etc.

Oils of lubricating viscosity also are used as transmission fluids, hydraulic fluids, industrial fluids, etc., and the novel features of the present invention are used to further improve the properties of these oils. During such use, the lubricity properties of the oil are important. Any suitable lubricating oil which is used for this purpose is improved by incorporating the additive of the present invention.

From the hereinbefore description, it will be seen that the present invention is directed to improving lubricating compositions. As mentioned above, the demand on lubricating oils is becoming more severe and is being met by the use of the improved additive. This increased severity is encountered, for example, in oils used for the lubrication of hypoid gears because of the high contact pressures encountered. More recent developments are directed to the extremely long time use of such oils as, for example, in the break-in or run-in oil used in automobile differential systems, during which period the gears are extremely susceptible to surface damage. The oil must protect the gear surfaces during the high torque-low speed low torque-high speed and high torque-high speed conditions. Furthermore, it is not necessary to change the oil after the break-in period, and the oil then is expected to operate satisfactorily for one year or more and 20,000 miles or

more of operation. In addition to retaining its lubricity properties, it is also desired to avoid corrosion of the metal parts and also to avoid the formation of deposits which could interfere with satisfactory operation. While the novel additives of the present invention are particularly useful in oils of lubricating viscosity required for more severe use, it is understood that the improved benefits also are obtained to oils of lubricating viscosity which are used under less severe conditions.

In one embodiment the present invention relates to a lubricating composition containing a stabilizing concentration of an inhibitor mixture of (1) a salt of an amine having from about 8 to about 40 carbon atoms per molecule and a carboxylic acid having from about 6 to about 50 carbon atoms per molecule and (2) a salt of an amine having from about 8 to about 40 carbon atoms per molecule and an alkyl acid phosphate in which at least one alkyl group contains from about 3 to about 20 carbon atoms.

In a specific embodiment the present invention relates to lubricating oil containing a stabilizing concentration of an inhibitor mixture of (1) salt of N-tallow-1,3-diaminopropane and dicarboxylic acid having from about 10 to about 50 carbon atoms per molecule, (2) salt of N-tallow-1,3-diaminopropane and mixed mono- and dioctyl acid orthophosphate and (3) a phenolic antioxidant.

From the hereinbefore embodiments, it will be seen that the present invention provides a novel additive mixture for use in lubricating compositions.

AMINE SALT OF CARBOXYLIC ACID

One component of the novel additive mixture of the present invention is an amine salt of a carboxylic acid. Any suitable amine may be employed and may comprise a primary monoamine, but preferably comprises a diamine and, still more particularly, an N-alkyl-diaminoalkane. Preferably, the amine contains at least 8 carbon atoms and, in general, will contain from about 12 to about 40 carbon atoms per molecule. Illustrative primary monoamines include octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, nonadecylamine, eicosylamine, etc. The amine may be prepared from fatty acid derivatives and thus may comprise tallow amine, hydrogenated tallow amine, lauryl amine, coconut amine, soya amine, etc.

Of the diamines, the N-alkyl-diaminoalkanes are preferred. A particularly preferred amine of this class comprises an N-alkyl-1,3-diaminopropane in which the alkyl group contains from about 8 to about 25 carbon atoms. A number of N-alkyl-1,3-diaminopropanes of this class are available commercially, such as "Duomeen T" and "Diam 26") in which the alkyl group is derived from tallow and contains from about 12 to about 20 carbon atoms per group, and mostly 16 to 18 carbon atoms. Other N-alkyl-1,3-diaminopropanes may be prepared to contain any number of carbon atoms desired in the alkyl group and thus the alkyl group is selected from hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, etc.

While the N-alkyl-1,3-diaminopropanes are preferred, it is understood that other suitable N-alkyl diaminoalkanes may be employed. Illustrative examples include N-alkyl-1,2-diaminoethane, N-alkyl-1,2-diaminopropane, N-alkyl-1,2-diaminobutane, N-alkyl-1,3-diaminobutane, N-alkyl-1,4-diaminobutane, N-alkyl-1,2-diaminopentane, N-alkyl-1,3-diaminopentane, N-alkyl-1,4-diaminopentane, N-alkyl-1,5-diaminopentane, N-alkyl-1,2-diaminohexane, N-alkyl-1,3-diaminohexane, N-alkyl-1,4-diaminohexane, N-alkyl-1,5-diaminohexane, N-alkyl-1,6-diaminohexane, etc. It is understood that a mixture of amines may be employed and also that the different amines are not necessarily equivalent but all of them may be used in the preparation of active additive compositions.

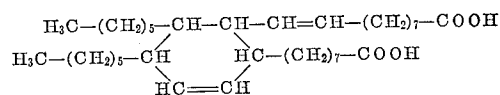
As hereinbefore set forth, the amine salt of a carboxylic

acid is used as one component of the additive mixture. Any suitable carboxylic acid may be used and preferably is a polybasic carboxylic acid. The carboxylic acid preferably contains at least 6 and still more preferably at least 10 carbon atoms per molecule and, more particularly, from about 20 to about 50 carbon atoms per molecule. Illustrative polybasic carboxylic acids include adipic, pimelic, suberic, azelaic, sebacic, phthalic, etc., aconitic, citric, etc., hemimellitic, trimesic, prehnitic, mellophanic, pyromellitic, mellitic, etc., and higher molecular polybasic carboxylic acids. It is understood that a mixture of acids may be employed.

A particularly preferred acid comprises a mixed by-product acid being marketed commercially under the trade name of "VR-1 Acid." This acid is a mixture of polybasic acids, predominantly dibasic, and is a residue produced by distilling, at about 270° C. under about 4 mm. of mercury pressure, the by-product acids obtained in the preparation of sebacic acid by fusing castor oil with alkali. Production of this residue is described in more detail in U. S. Patent 2,267,269 to Cheetham et al. In the manufacture of sebacic acid from castor oil, the oil is heated with a caustic alkali. This splits the oil, forming octanol-2, methylhexyl ketone, the alkali salt of sebacic acid, and the alkali salts of various other long-chained acids. The alcohol and ketone are readily removed from the reaction mixture by distillation. The alkali salts which remain then are dissolved in water and, on upon slight acidification of the resulting solution, an oily layer separates. At a pH of about 6, the aqueous phase contains the alkali salt of sebacic acid, while the oily layer contains various other acids from the reaction. The term "by-product acids" is generally applied to the mixture of acids forming the oily layer.

These by-product acids then are separated into two parts. After these acids have been washed with a dilute mineral acid, such as sulfuric or hydrochloric, they are washer with water and dried. They then are distilled under reduced pressure. Fatty acids which are primarily monobasic carboxylic acids are taken off at 100° C. to 270° C. at pressures as low as 4 mm. This treatment leaves a residue which is a mixture of fatty acids, apparently primarily polybasic in character. The residue is commercially available from Rohm & Haas Company under the trade name of "VR-1 Acid" and has an average molecular weight of 500-600, an acid number of 134-160, a saponification number of 174-179, and an iodine number of 53-60. Another mixed acid of substantially the same composition is available commercially under the trade name of "D50ME Acid."

Another preferred acid comprises a mixed acid being marketed commercially under the trade name of "Empol 1022." This dimer acid is a dilinoleic acid and is represented by the following general formula:



This acid is a viscous liquid, having an apparent molecular weight of approximately 600. It has an acid value of 180-192, an iodine value of 80-95, a saponification value of 185-195, a neutralization equivalent of 290-310, a refractive index at 25° C. of 1.4919, a specific gravity at 15.5° C./15.5° C. of 0.95, a flash point of 530° F., a fire point of 600° F., and a viscosity at 100° C. of 100 centistokes.

While the polycarboxylic acids generally are preferred, in another embodiment of the invention a monocarboxylic acid may be used or a mixture of a monocarboxylic acid and the polycarboxylic acid hereinbefore set forth. Here, again, it is preferred that the carboxylic acid contains at least 6 atoms per molecule and may range up to 50 carbon atoms per molecule. Illustrative monocarboxylic acids include caproic, heptylic, caprylic, pel-

argonic, carpic, lauric, myristic, palmitic, steric, arachidic, benhenic, lignoeric, cerotic, etc., decalenic, dodecalenic, palmitoleic, oleic, ricinoleic, petroselinic, vacenic, linoleic, linolenic, eleostearic, licanic, parinaric, gadoleic, arachidonic, cetoleic, erucic, selacholeic.

Here, again, mixtures of such acids are available commercially at lower cost and advantageously are used in preparing the additive of the present invention. A particularly preferred mixture is tall oil acid which comprises a mixture of saturated and unsaturated fatty acids and rosin acids and is obtained by acidifying the black liquor skimmings obtained in the pulping of wood. The manufacture of tall oil acid is described in the Encyclopedia of Chemical Technology, volume 13, pages 572-577. A number of typical American tall oil acids are shown on page 575 of this encyclopedia, along with typical properties thereof.

While the crude tall oil acid may be used in accordance with the present invention, it is preferable to use a purified tall oil acid. A particularly satisfactory tall oil acid is available commercially under the trade name of "Indusoil L-5." This acid has the following typical properties:

| Specifications | Minimum | Maximum |
|----------------------------|---------|---------|
| Color, Gardner | | 7 |
| Acid No. | 188 | 196 |
| Saponification No. | 190 | 198 |
| Fatty acids, percent | 90 | |
| Rosin acids, percent | | 5 |
| Unsaponifiables, percent | | 4 |
| Specific gravity, 60F/60F | 0.905 | 0.910 |
| Pour Point, ° F | 45 | 55 |
| Flash Point, Open Cup, ° F | 360 | 400 |
| Fire Point, Open Cup, ° F | 410 | 440 |

When a mixture of the monocarboxylic acid and the polycarboxylic acid is used, both being selected from those hereinbefore set forth, it generally is preferred to use these in a ratio of one equivalent of each with two equivalents of the amine. However, in some cases, an excess of one acid may be employed and thus may range up to ten or more equivalents of the monocarboxylic acid with one equivalent of the polycarboxylic acid, or up to ten or more equivalents of the polycarboxylic acid with one equivalent of the monocarboxylic acid.

The amine salt of carboxylic acid is prepared in any suitable manner. In general, the salt is readily prepared by admixing the amine and carboxylic acid at ambient temperature, preferably with vigorous stirring. Elevated temperature may be employed, but generally will not exceed about 250° F. When desired, the salt may be prepared in the presence of a solvent for ease in handling, either of the amine and/or acid or of the final mixture. Any suitable solvent may be employed and may comprise an aromatic hydrocarbon such as benzene, toluene, xylene, ethylbenzene, etc., or a mixture such as naphtha, which may be straight run, catalytically cracked, thermally reformed, catalytically reformed, preferably in the presence of hydrogen or mixtures thereof, or lubricating oil. Depending upon the particular lubricating composition in which the inhibitor mixture is employed, the lower boiling solvent may be removed by fractionation or it may be allowed to remain in the additive mixture. When desired, the additive mixture will be marketed as a solution in a suitable solvent and the same solvent used in the final mixture also may be used during the preparation of the amine-carboxylic acid salt.

In general, the neutral salt of the amine and carboxylic acid is preferred. The neutral salt is prepared by utilizing stoichiometric amounts of the carboxylic acid and amine. In other words, the concentrations of the carboxylic acid and amine are selected so that there is an equivalent number of carboxylic acid groups to amine

groups. In another embodiment the salt may be a basic salt, which is prepared by utilizing a deficiency of carboxylic acid groups in relation to the amino group as, for example, by utilizing one equivalent of carboxylic acid per two equivalents of amine. In still another embodiment, an acid salt may be employed, which may be prepared by using an excess of acid with relation to the amine as, for example, two equivalents of acid per one equivalent of amine. It is understood that these different salts are not necessarily equivalent.

AMINE SALT OF ALKYL ACID PHOSPHATE

In preparing the amine salt of the alkyl acid phosphate, the amine is selected from the amines hereinbefore specifically set forth in the description of the amine salt of carboxylic acid. In the interest of simplicity, these amines are not repeated here, but it is understood that the amine is selected from those hereinbefore specifically set forth.

In one embodiment, the amine used in the preparation of the salt of the alkyl acid phosphate is the same amine as used in the preparation of the amine salt of the carboxylic acid. In another embodiment, a different amine is used in the preparation of each of these salts, but the amines preferably are selected from those hereinbefore specifically set forth.

Any suitable alkyl acid phosphate is used in preparing the salt. The term "alkyl acid phosphate" includes both the alkyl acid orthophosphates and the alkyl acid pyrophosphates. In the alkyl acid orthophosphates, the monoalkyl ester, dialkyl ester or a mixture thereof may be employed. In the alkyl acid pyrophosphates, the monoalkyl ester, dialkyl ester, trialkyl ester or mixtures thereof may be employed, the dialkyl ester being preferred and the ester groups being attached to the same or different phosphorous atoms. Generally, however, this compound will be symmetrical and, thus, the alkyl ester groups will be attached to different phosphorous atoms.

At least one of the alkyl groups constituting the ester portion of the alkyl acid phosphate contains at least 3 and preferably at least 5 carbon atoms and contains up to 20 and preferably up to 12 carbon atoms. Illustrative examples of preferred alkyl acid orthophosphates include monoamyl acid orthophosphate, diamyl acid orthophosphate, monohexyl acid orthophosphate, dihexyl acid orthophosphate, monoheptyl acid orthophosphate, diheptyl acid orthophosphate, monooctyl acid orthophosphate, dioctyl acid orthophosphate, monononyl acid orthophosphate, dinonyl acid orthophosphate, monodecyl acid orthophosphate, didecyl acid orthophosphate, monoundecyl acid orthophosphate, diundecyl acid orthophosphate, monododecyl acid orthophosphate, didodecyl acid orthophosphate. As hereinbefore set forth, these are preferred alkyl acid phosphates. However, it is understood that the alkyl group or groups may contain from about 3 to about 12 carbon atoms.

Preferred alkyl acid pyrophosphates include monoamyl acid pyrophosphate, diamyl acid pyrophosphate, monohexyl acid pyrophosphate, dihexyl acid pyrophosphate, monoheptyl acid pyrophosphate, diheptyl acid pyrophosphate, monooctyl acid pyrophosphate, dioctyl acid pyrophosphate, monononyl acid pyrophosphate, dinonyl acid pyrophosphate, monodecyl acid pyrophosphate, didecyl acid pyrophosphate, monoundecyl acid pyrophosphate, diundecyl acid pyrophosphate, monododecyl acid pyrophosphate. Here, again, it is understood that the alkyl pyrophosphates may contain from about 3 to about 20 carbon atoms in the alkyl group or groups.

Alkyl acid phosphates are manufactured commercially as a mixture of the mono- and di-alkyl acid phosphates and such mixtures are available commercially at a lower cost. As another advantage of the present invention, such lower cost mixtures may be used in preparing the additive of the present invention. Particularly preferred mixed alkyl acid phosphates comprise a

mixture of mono- and di-isoamyl acid orthophosphate, a mixture of mono- and di-isoctyl acid orthophosphate and the corresponding mixed alkyl acid pyrophosphates.

The amine-alkyl acid phosphate salt is prepared in any suitable manner. In general, this salt is prepared in substantially the same manner as the amine-carboxylic acid salt as hereinbefore described. The amine and alkyl acid phosphate are commingled, either at ambient temperature or slightly elevated temperature, with vigorous stirring. When employed, the elevated temperature generally will not exceed about 250° F. Here, again, a solvent may be used for ease in handling and the solvent is selected from those hereinbefore specifically set forth.

In general, the neutral salt of the alkyl acid phosphate and amine is preferred. The neutral salt is prepared by utilizing stoichiometric amounts of the alkyl acid phosphate and the amine. In other words, the concentration of alkyl acid phosphate and amine will be selected so that there will be an equivalent number of acid groups to amino groups. Thus, the specific concentrations will depend upon whether the orthophosphate or pyrophosphate salt is prepared and whether a monoamine or polyamine is used. In another embodiment, the salt is a basic salt, which is prepared by utilizing a deficiency of acid groups in relation to the amino group as, for example, by utilizing one equivalent of acid per two equivalents of amine. In still another embodiment, an acid salt is employed, which is prepared by using an excess of acid with relation to the amine as, for example, two equivalents of acid per one equivalent of amine. It is understood that these different salts are not necessarily equivalent.

In the preparations described above, the amine salt of the carboxylic acid and the amine salt of the alkyl acid phosphate are separately formed and then are commingled in the desired proportions. In another embodiment, the amine salts may be prepared in a single step. In this embodiment, the carboxylic acid and the alkyl acid phosphate are commingled, preferably with vigorous stirring, and then the amine or amines are added thereto with vigorous stirring. The reaction is effected at ambient temperature, or an elevated temperature which generally will not exceed about 250° F. may be employed. In cases where the amine is a solid at ambient temperature, the amine may be heated up to about 250° F. in order to melt the same and the melted amine then is added to the acids as aforesaid.

PHENOLIC ANTIOXIDANT

In a preferred embodiment of the invention, a phenolic antioxidant is incorporated in the additive mixture. Any suitable phenolic antioxidant may be employed. Preferred phenolic antioxidants include tertiarybutylcatechol, 2,6-ditertiarybutyl-4-methylphenol, 2,4-dimethyl-6-tertiarybutylphenol, etc., 2-tertiarybutyl-4-methoxyphenol, 2,6-ditertiarybutyl-4-methoxyphenol, 2-tertiarybutyl-4-ethoxyphenol, 2,6-ditertiarybutyl-4-ethoxyphenol, etc. It is understood that any suitable phenolic antioxidant may be used in the additive mixture of the present invention.

The amine salt of carboxylic acid and amine salt of alkyl acid phosphate are used in any suitable proportions in the additive mixture. These proportions may range from 5% by weight of one component to 95% by weight of the other component. Preferably at least 10% of one salt is included in the mixture and, in a particularly preferred embodiment, the salts are used in a proportion of 30% by weight of one salt and 70% by weight of the other salt. When employed, the phenolic antioxidant is used in a concentration of from about 1% to about 40% by weight and preferably from about 1% to about 10% by weight of the additive mixture. Thus, the additive mixture will comprise from 5% to about 95% by weight of the amine salt of carboxylic acid, from about 5% to about 95% by weight of the amine salt of alkyl acid phosphate and from about 1% to about 40% by weight of the phenolic antioxidant. In a preferred method of manu-

facture, the amine salts are first prepared and the phenolic antioxidant then is incorporated therein.

As hereinbefore set forth, the novel additive mixture of the present invention is incorporated in a lubricating composition. In addition to maintaining the lubricity properties of the oil during use under severe conditions, the additive mixture of the present invention offers the advantage that it is not detrimentally affected by the presence of water. While generally it is desirable to exclude water in lubricating oils, in many cases water inadvertently enters the lubricating oil. As will be shown by the examples appended to the present specifications, the presence of water does not adversely affect the additive mixture. Another advantage to the novel additive mixture of the present invention is that it is readily soluble in lubricating oil and, therefore, will remain in solution during use.

Lubricating oils generally have a viscosity within the range of from 10 SUS at 100° F. to 1000 SUS at 210° F. (SAE viscosity numbers include the range from SAE 10 to SAE 160). The petroleum oils are obtained from paraffinic, naphthenic, asphaltic or mixed base crudes. As mentioned above, the novel additive mixture of the present invention is readily soluble in lubricating oils, even the highly paraffinic lubricating oils.

The novel additive mixture of the present invention is used in a small but stabilizing concentration in the lubricating composition. In conventional lubricating oil, the additive mixture is employed in a concentration of from about 0.01% to about 2% by weight of the oil. When used in lubricating oil for more severe operations, such as hypoid gear oil, the additive mixture is used in a concentration of from about 1% to about 20% or more by weight of the oil. In general, substantially the same range of inhibitor concentration is employed when the oil is used as transmission fluid, hydraulic fluid, industrial fluid, etc.

The following examples are introduced to illustrate further the novelty and utility of the present invention, but not with the intention of unduly limiting the same.

As hereinbefore set forth, the novel additive mixture of the present invention serves to stabilize the lubricity properties of the lubricating oil, and the effectiveness of the additive mixture for this purpose has been determined in a modified Bowden-Leben pin and disc machine. The Bowden-Leben method is described in "The Friction and Lubrication of Solids," 1954, page 74, by Bowden and Tabor. This method is also discussed in the article by E. Rabinowicz entitled "The Boundary Friction of Very Well Lubricated Surfaces," which was presented at the A.S.L.E. Ninth Annual Meeting in Cincinnati on April 5, 1954, and published in the July-August 1954 issue of "Lubricating Engineering." In the modification used for the runs reported herein, a highly polished steel disc rotates in contact with an upwardly extended rounded steel pin. The pin and disc then are immersed in a pan containing the oil to be evaluated. The equipment is enclosed in a housing which is heated for varying the temperature of the run which, in these experiments, ranged from 72° to 350° F. The equipment also includes a variable speed reducer for varying the r.p.m. of the disc and also includes means for varying the load. In each run the wear or break-in period consists of gradually increasing the speed to 196 r.p.m. at 2000 g. load and decreasing the speed to 12 r.p.m. after which the speed is increased to 196 r.p.m. The load is varied from 500 g. to 2000 g. and the coefficient of friction was determined at r.p.m.'s decreasing from 196 to 0.1. A strain gage circuit is used as sensing element in converting the frictional effects into equivalent electrical responses which then are recorded on a continuous chart recorder. The highest coefficient of friction is reported for each run. In addition, the diameter of the wear spot on the pin is measured. The pin, disc and pan are visually inspected immediately after the test to determine visible corrosion

and also to determine whether deposit formation has occurred.

The lubricating oil used in the runs reported in the following examples is a commercial white oil sold by A. H. Carnes Company as "Carnes 340 White Oil." Typical specifications of this oil include the following:

| | |
|----------------------------------|---------|
| Distillation range, ° F. ----- | 740-975 |
| Specific gravity at 60° F. ----- | 0.8836 |
| Viscosity: | |
| At 100° F., SUS ----- | 360 |
| At 210° F., SUS ----- | 52.2 |
| Flash point, COC, ° F. ----- | 440 |
| Pour point, ° F. ----- | -20 |
| Refractive index at 20° C. ----- | 1.4805 |
| Saybolt color ----- | +30 |

Example I

The additive mixture of this example comprised 50% by weight of the neutral salt of "Diam 26" and "D50ME Acid" and 50% by weight of the neutral salt of "Diam 26" and mixed mono- and di-isooctyl acid orthophosphates. As hereinbefore set forth, "Diam 26" is N-tallow-1,3-diamino-propane and contains predominantly 16 to 18 carbon atoms in the tallow group. Also, as hereinbefore set forth, "D50ME Acid" is of substantially the same composition as "VR-1 Acid." The mixed mono- and di-isooctyl acid orthophosphates are available commercially.

The additive mixture was prepared as follows. For ease in handling, the preparation was made in admixture with a paraffinic oil available commercially as "Sinco 54" from the Sinclair Refining Company. This oil has an API gravity at 60° F. of 30° and a viscosity at 210° F. of 53-58 SUS. The neutral salts were prepared in a single step operation by adding 168 g. of "D50ME Acid" and 153 g. of mixed mono- and di-octyl acid orthophosphate to 1832 g. of the paraffinic oil at room temperature, with intimate stirring. 188 g. of "Diam 26" amine were heated to about 125° F. to melt the same and then the melt was added gradually to the mixture of acids with intimate stirring. The product consisted of a solution containing 22.5% by weight of active ingredients and was recovered as a fluid tan liquid.

The lubricity properties of the Carnes 340 White Oil, with and without additives, were evaluated in the manner described above. The following table reports the results of evaluating a sample of the Carnes 340 White Oil not containing an additive of the present invention (Run No. 1) and may be considered as the blank or control run.

Run No. 2 in the following table was made with a sample of the Carnes 340 White Oil containing 1% by weight (active ingredient basis) of the mixture of "Diam 26" amine neutral salt of "D50ME Acid" and "Diam 26" amine neutral salt of mono- and di-octyl acid orthophosphates.

As hereinbefore set forth, the additive mixture of the present invention is not adversely affected by water and this is illustrated in Run No. 3 which is a duplicate of Run No. 2, except that 1% by weight of water was added to the mixture.

As hereinbefore set forth, Run No. 1 is the blank or control run of the oil without an additive mixture of the present invention. The "S" indicates "slip stick" or "seizure." Accordingly, it will be noted that the uninhibited oil was unsatisfactory for use under the conditions of evaluation.

Run No. 2 was made using the additive mixture of the present invention and experienced no seizure during the complete temperature range and, in fact, the coefficient of friction was very low. Also, it will be noted that the area of wear was considerably low than the 0.532 mm.² difference observed in the blank or control run.

Run No. 3 was made utilizing 1% by weight of the additive mixture, but also contained 1% by weight of water. It will be noted that the water did not increase the coefficient of friction and that no seizure occurred during the entire range of operation. However, deposit formation occurred in both Runs 1 and 3, but no deposits occurred in Run No. 2.

Example II

The additive mixture of this example comprised one-third by weight of the neutral salt of "Duomeen T" and "D50ME Acid," one-third by weight of the neutral salt of "Duomeen T" and mixed mono- and di-isooctyl acid orthophosphates and one-third by weight of 2,6-di-tertiarybutyl-4-methylphenol as the phenolic antioxidant. The phenolic antioxidant was used in a high concentration in these runs in order to make sure that no detrimental effects were obtained by the phenolic antioxidant.

The additive mixture of this example was prepared as follows. The neutral salt of "Duomeen T" and "D50ME Acid" was prepared by admixing the amine and acid at room temperature, with intimate stirring. The neutral salt of "Duomeen T" and mono- and di-isooctyl acid orthophosphate was prepared separately by mixing the amine and alkyl acid phosphate at room temperature, with intimate stirring. 20 g. of the "Duomeen T" salt of "D50ME Acid" and 20 g. of the amine salt of alkyl acid phosphate were commingled at room temperature. 2,6-di-tertiarybutyl-4-methylphenol is a white powder and 20 g. thereof were dissolved in 40 g. of a paraffinic oil available commercially from the American Oil Company as "Paraffin Oil No. 11." This oil has an API gravity of 26.5-29.5° and a viscosity at 100° F. of 100-110 SUS. The mixture of 2,6-di-tertiarybutyl-4-methylphenol and "Paraffin Oil No. 11" was heated to about 125° F. in order to form a homogeneous solution and the solution then was added gradually, with intimate stirring, to the mixture of the "Duomeen T" salt of "D50ME Acid" and the "Duomeen T" salt of alkyl acid phosphate. The mixture was vigorously stirred in order to obtain a homogeneous solution which was recovered as a tan colored liquid.

The additive mixture prepared in the above manner was evaluated in the Carnes 340 White Oil in the same manner as hereinbefore described and the results are reported in the following table.

For comparison purposes, Run No. 1, which is the blank or control run, is repeated in the following table.

Run No. 4 contained 1.6% by weight (active ingredient basis) of the additive mixture described above.

TABLE I

| Run No. | Water Present | Coefficient of Boundary Friction | | | | | | | Area of Wear Spot on Pin, mm. ² | | |
|---------|---------------|----------------------------------|---------|---------|---------|---------|---------|---------|--|-------|------------|
| | | 72° F. | 100° F. | 150° F. | 200° F. | 250° F. | 300° F. | 350° F. | Original | Final | Difference |
| 1.----- | No.----- | 0.18-S | 0.24-S | 0.24-S | >0.24-S | >0.24-S | >0.24-S | ----- | 0.102 | 0.635 | 0.532 |
| 2.----- | No.----- | 0.08 | 0.09 | 0.09 | 0.09 | 0.07 | 0.06 | ----- | 0.219 | 0.321 | 0.102 |
| 3.----- | Yes.----- | 0.08 | 0.08 | 0.07 | 0.08 | 0.05 | ----- | <0.04 | 0.321 | 0.366 | 0.045 |

Run No. 5 is a duplication of Run No. 4, except that 1% by weight of water was added to the oil.

TABLE II

| Run No. | Coefficient of Boundary Friction | | | | | | | Area of Wear Spot on Pin, mm. ² | | |
|---------|----------------------------------|---------|---------|---------|---------|---------|---------|--|-------|------------|
| | 72° F. | 100° F. | 150° F. | 200° F. | 250° F. | 300° F. | 350° F. | Original | Final | Difference |
| 1..... | 0.18-S | 0.24-S | 0.24-S | >0.24-S | >0.24-S | >0.24-S | <0.04 | 0.102 | 0.635 | 0.532 |
| 4..... | | 0.09 | | 0.09 | | | <0.04 | 0.159 | 0.219 | 0.060 |
| 5..... | | 0.07 | | 0.07 | 0.04 | | <0.04 | 0.219 | 0.219 | |

Here, again, it will be noted that the additive mixture of the present invention was very effective in maintaining the lubricity properties of the oil during the evaluation. There was no seizure and, in fact, the coefficient of friction was very low. Also, the area of wear spot was low.

Run No. 5 demonstrates that the additive mixture of this example was not detrimentally affected by the presence of water.

In both Runs No. 4 and 5 there was no deposit formation. The addition of the phenolic antioxidant served to avoid the deposit formation in the presence of water.

Example III

The additive mixture of this example comprised 45.5% by weight of the neutral salt of "Duomeen T" and "D50ME Acid", 45.5% by weight of the neutral salt of "Duomeen T" and mono- and di-octyl acid orthophosphates and 9% by weight of 2,6-ditertiarybutyl-4-methylphenol. This additive mixture was made by the simultaneous formation of the "Duomeen T" salts of "D50ME Acid" and of octyl acid orthophosphates as described in Example I. After formation of the mixed salts, the mixture is heated to about 105° F. and the phenolic antioxidant then is added with intimate stirring.

The additive mixture prepared in the above manner is incorporated in a concentration of 5% by weight in "Trojan MP No. 90" oil for use as hypoid gear oil. The addition of the additive mixture of this example to the hypoid gear oil serves to retain the lubricity properties of the oil during such use and also retards the formation of deposits.

Example IV

The additive mixture of this example comprises 20% by weight of the acid salt of "Diam 26" amine and "VR-1 Acid" and 80% by weight of the neutral salt of "Diam 26" amine and the mixed mono- and di-tridecyl acid pyrophosphates. The additive mixture is prepared by first separately formulating each of the salts and then compositing the salts to form the mixture of the composition mentioned above.

The additive mixture prepared in the above manner is utilized in a concentration of 1% by weight as an additive in lithium grease. The grease is prepared by mixing 91% of a highly refined Pennsylvania oil having a Saybolt viscosity of 180 seconds at 100° F. with 8% of lithium stearate. The mixture is heated to about 450° F. with agitation. Subsequently, the grease is cooled to 320° F. while agitating and, at this temperature, 1% by weight of the additive mixture of the present invention is added. Agitation is continued and the mixture then is allowed to cool to about 250° F. and finally cooled slowly to room temperature.

Example V

The additive mixture of this example comprises 75% by weight of the N-soya-1,3-diaminopropane neutral salt of "Empol 1022 Acid" and 25% by weight of the neutral salt of heptylamine and mixed mono- and di-isoamyl acid orthophosphates. Each of the salts is separately prepared and then are composited in the proper proportion to form the additive mixture described above.

The additive mixture prepared in the above manner is used in a concentration of 2.5% by weight in di-(2-

ethylhexyl) sebacate marketed under the trade name of "Plexol 201." This material was used as a synthetic lubricating oil and the incorporation of the additive mixture therein serves to stabilize the lubricity properties of the lubricant during use.

Example VI

The additive mixture of this example comprises 49% by weight of the neutral salt of tallow amine and tall oil acid, 49% by weight of the neutral salt of tallow amine and mixed mono- and di-decyl acid orthophosphates and 2% by weight of 2,4-dimethyl-6-tertiarybutylphenol. The additive mixture is prepared by first commingling the tall oil acid and decyl acid orthophosphates at room temperature with stirring and then gradually adding, with stirring, the tallow amine in a concentration to form the neutral salts. The phenolic antioxidant then is added to the mixture and the stirring is continued to completely dissolve the phenolic antioxidant.

The additive mixture prepared in the above manner is utilized in a concentration of 0.5% by weight as an additive in crank-case oil.

We claim as our invention:

1. Lubricating composition comprising a major proportion of lubricating oil and from about 0.01% to about 20% by weight of an additive mixture of (1) from about 5% to about 95% by weight of a salt of N-alkyl-1,3-diaminoalkane in which said alkyl contains at least 8 carbon atoms and dicarboxylic acid having at least 6 carbon atoms and (2) from about 5% to about 95% by weight of a salt of N-alkyl-diaminoalkane in which said alkyl contains at least 8 carbon atoms and alkyl acid phosphate in which at least 1 alkyl group contains at least 3 carbon atoms.

2. The composition of claim 1 in which said additive mixture also contains from about 1% to about 40% by weight of a phenolic antioxidant.

3. Lubricating oil comprising a major proportion of lubricating oil and from about 0.01% to about 20% by weight of an additive mixture of (1) from about 5% to about 95% by weight of a salt of N-tallow-1,3-diaminopropane and dicarboxylic acid having from about 10 to about 50 carbon atoms and (2) from about 5% to about 95% by weight of a salt of N-tallow-1,3-diaminopropane and mixed mono- and di-alkyl acid orthophosphates.

4. The composition of claim 3 wherein said mixed phosphates are mixed mono- and di-octyl acid orthophosphates.

5. The composition of claim 3 in which said additive mixture also contains from about 1% to about 40% by weight of a phenolic antioxidant.

6. Lubricating oil comprising a major proportion of lubricating oil and from about 0.01% to about 20% by weight of an additive mixture of (1) from about 5% to about 95% by weight of a salt of N-tallow-1,3-diaminopropane and dicarboxylic acid having from about 10 to about 50 carbon atoms, (2) from about 5% to about 95% by weight of a salt of N-tallow-1,3-diaminopropane and mixed mono- and di-isoctyl acid orthophosphates and (3) 2,6-ditertiarybutyl-4-methylphenol antioxidant.

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