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OIL OF LUBRICATING VISCOSITY

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This invention relates to an oil of lubricating viscosity of improved properties.

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 axelate, 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 tricarballylate, 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, tetraisooctyl 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 heptane, trimethylol octane, trimethylol decane, 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, tridecyclphosphate, 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.

Oils of lubricating viscosity also are used as cutting oils, rolling oils, soluble oils, drawing compounds, etc. In this application, the oil is used as such or as an emulsion with water. Here, again, it is desired that the oil serves to lubricate the metal parts of saws, knives, blades, rollers, etc., in addition to dissipating the heat created by the contact of the moving metal parts.

Oils of lubricating viscosity also are used as slushing oils. The slushing oils are employed to protect finished or unfinished metal articles during storage or transportation from one area to another. The metal articles may be of any shape or form including steel sheets, plates, panels, coils, bars, etc., which may comprise machine parts, engines, drums, piston rings, light arms, etc., as well as farm machinery, marine equipment, parts for military or other vehicles, household equipment, factory equipment, etc. A coating which may be visible to the eye, or not, as desired, covers the metal part and protects it from corrosion, etc.

From the hereinbefore discussion, it will be seen that the present invention is directed to improving oils of lubricating viscosity which have a variety of uses. 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

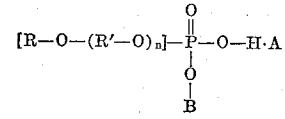
one year or more and 20,000 miles or more of operation. In addition to retaining its lubricity properties, it is also desired to avoid corrosion of the metal parts and also to avoid the formation of deposits which could interfere with satisfactory operation. While the novel additives of the present invention 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 an oil of lubricating viscosity suitable for use as lubricating oil, transmission fluid, cutting oil and slushing oil, comprising a major proportion of lubricating oil and a small but stabilizing proportion of amine salt of oxyalkylenated hydroxyhydrocarbon phosphate.

In a specific embodiment the present invention relates to a lubricating oil containing a small but stabilizing proportion of diamine salt of polyoxyalkylenated alkylphenol phosphate.

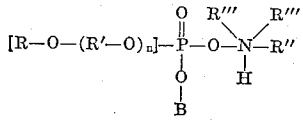
The amine salts of oxyalkylenated hydroxyhydrocarbon phosphates are believed to be new compositions of matter and, accordingly, are so being claimed in the present application.

As hereinbefore set forth, the additive for use in the present invention is an amine salt of an oxyalkylenated hydroxyhydrocarbon phosphate. The additive is illustrated by the following general formula:



where O is oxygen, P is phosphorus, H is hydrogen, *n* is an integer of from 1 to 40, R is a hydrocarbon group, R' is alkylene, A is amine, B is selected from the group consisting of hydrogen, the same as the bracketed group, and the same as A.

The general formula hereinbefore set forth also may be illustrated as follows:



where the symbols have the same meaning as set forth above, N is nitrogen, R'' is a hydrocarbon or substituted hydrocarbon group, and R''' is hydrogen, a hydrocarbon or substituted hydrocarbon group.

In a preferred embodiment R is selected from alkylphenyl and aliphatic groups. In the alkylphenyl species, 1, 2 or 3 alkyl groups of from 4 to 30 and, more particularly, from 6 to 15 carbon atoms each, will be attached to the phenyl ring. Illustrative preferred alkylphenyl groups include hexylphenyl, heptylphenyl, octylphenyl, nonylphenyl, decylphenyl, undecylphenyl, dodecylphenyl, tridecylphenyl, tetradecylphenyl, pentadecylphenyl, etc., dihexylphenyl, diheptylphenyl, dioctylphenyl, dinonylphenyl, didecylphenyl, diundecylphenyl, didodecylphenyl, etc., trihexylphenyl, triheptylphenyl, trioctylphenyl, trinonylphenyl, tridecylphenyl, etc. In another embodiment the alkylphenyl radical may contain one or more alkyl groups containing 4 to 30 carbon atoms and one or more alkyl groups containing less than 4 carbon atoms and selected from methyl, ethyl and propyl. When one alkyl group is attached to the phenyl ring, it preferably is in the position para to the oxygen. When two alkyl groups are attached to the phenyl ring, they preferably are in the 2,4- or 3,5-positions.

Where R is an aliphatic group, it preferably contains from 6 to 40 carbon atoms and, more particularly, from 10 to 30 carbon atoms. Illustrative preferred aliphatic groups include decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, etc. In general, it is preferred that the aliphatic group is saturated. In another embodiment, the aliphatic group may be unsaturated and will be selected from olefinic radicals corresponding to the saturated radicals hereinbefore specifically set forth. The aliphatic group may be straight chain or may contain branching in the chain.

R' in the above general formula is an alkylene group and may contain from 1 to 10 and preferably from 2 to 4 carbon atoms per group. The preferred alkylene radicals thus are ethylene, propylene and butaylene. As hereinbefore set forth, *n* is an integer of from 1 to 40 and preferably of from 2 to 12.

As hereinbefore set forth, the novel additive of the present invention is an amine salt of the oxyalkylenated hydroxyhydrocarbon phosphate. Referring to the above general formula, when B is hydrogen, or the same as A, the additive comprises the amine salt of the mono-(alkylenated hydroxyhydrocarbon) phosphate. When B in the above general formula is the same as the bracketed group (oxyalkylenated hydroxyhydrocarbon), the additive of the present invention comprises the amine salt of the di-(alkylenated hydroxyhydrocarbon) phosphate. It is understood that a mixture of the amine salt of the mono-(alkylenated hydroxyhydrocarbon) phosphate and of the amine salt of the di-(alkylenated hydroxyhydrocarbon) phosphate may be employed and also that a mixture of different amines may be used in preparing these additives.

Any suitable amine may be used and contains from 2 to 50 carbon atoms or more and preferably from 8 to 20 carbon atoms. The amine may be a monoamine or polyamine. Preferred monoamines include octyl amine, nonyl amine, decyl amine, undecyl amine, dodecyl amine, tridecyl amine, tetradecyl amine, pentadecyl amine, hexadecyl amine, heptadecyl amine, octadecyl amine, nonadecyl amine, eicosyl amine, etc. The amines 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 polyamines, 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 diaminoalkanes 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. Other polyamines include ethylenediamine, propylenediamine, butylene diamine, pentylenediamine, hexylenediamine, heptylenediamine, octylenediamine, etc., diethylenetriamine, dipropylenetriamine, dibutylenetriamine, dipentylenetriamine, dihexylenetriamine, diheptylenetriamine, dioctylenetriamine, etc., triethylenetetramine, tripropylenetetramine, tributylenetetramine, tripentylenetetramine, trihexylenetetramine, triheptylenetetramine, trioctylenetetramine, etc., tetraethylenepentamine, tetrapropylenepentamine, tetrabutylenepentamine, tetrahexylene-

pentamine, tetraheptylenepentamine, tetraoctylenepentamine, etc., pentaethylenehexamine, pentapropylenehexamine, pentabutylenehexamine, pentapentylenehexamine, pentahexylenehexamine, pentaheptylenehexamine, pentaoctylenehexamine, etc.

In another embodiment the amine is an aromatic amine. Aromatic monoamines include aniline, toluidines, xylidines, etc., naphthylamine, anthracylamine, rosin amine, etc., as well as the N-mono- and N,N-di-alkylated aromatic amines in which the alkyl group or groups contain from 1 to 15 carbon atoms or more. Illustrative examples of such compounds include N-methylaniline, N,N-di-methylaniline, N-ethylaniline, N,N-di-ethylaniline, N-propylaniline, N,N-di-propylaniline, N-butylaniline, N,N-di-butylaniline, N-amylaniline, N,N-di-amylaniline, N-hexylaniline, N,N-di-hexylaniline, N-heptylaniline, N,N-di-heptylaniline, N-octylaniline, N,N-di-octylaniline, N-nonylaniline, N,N-di-nonylaniline, N-decylaniline, N,N-decylaniline, N-undecylaniline, N,N-di-undecylaniline, N-dodecylaniline, N,N-di-dodecylaniline, etc., as well as the corresponding substituted toluidines, xylidines, naphthylamine, anthracylamines, etc.

In still another embodiment the amine may contain halogen as, for example, in compounds such as chloroaniline, 2,3-dichloroaniline, 2,4-dichloroaniline, 2,5-dichloroaniline, 2,6-dichloroaniline, 3,4-dichloroaniline, 3,5-dichloroaniline, bromoaniline, 2,3-dibromoaniline, 2,4-dibromoaniline, 2,5-dibromoaniline, 2,6-dibromoaniline, 3,4-dibromoaniline, 3,5-dibromoaniline, etc.

In another embodiment the aromatic amine is an arylamine including, for example, diphenylamine, aminodiphenylamine, diaminodiphenylamine, dinaphthylamine, aminodinaphthylamine, diaminodinaphthylamine, etc. In the polyamino aromatic compounds, the nitrogen atoms may be in the position ortho, meta or para to each other. The amino or diaminodiphenylamines may contain alkyl groups attached to one or both nitrogen atoms and the alkyl groups may contain from 1 to 20 or more carbon atoms each. Illustrative compounds include p,p'-di-methylaminodiphenylamine, p,p'-di-ethylaminodiphenylamine, p,p'-di-propylaminodiphenylamine, p,p'-di-butylaminodiphenylamine, p,p'-di-amylaminodiphenylamine, p,p'-dihexylaminodiphenylamine, p,p'-di-heptylaminodiphenylamine, p,p'-di-octylaminodiphenylamine, p,p'-di-nonylaminodiphenylamine, p,p'-di-decylaminodiphenylamine, etc., o,p'-di-methylaminodiphenylamine, o,p'-di-ethylaminodiphenylamine, o,p'-di-propylaminodiphenylamine, o,p'-di-butylaminodiphenylamine, o,p'-di-amylaminodiphenylamine, o,p'-di-hexylaminodiphenylamine, o,p'-diheptylaminodiphenylamine, o,p'-di-octylaminodiphenylamine, o,p'-di-nonylaminodiphenylamine, o,p'-di-decylaminodiphenylamine, etc., N-alkyldiaminodiphenylamine, N,N,N'-trialkyldiaminodiphenylamine, N,N,N'N'-tetralkyldiaminodiphenylamine, etc.

In still another embodiment the amine comprises such compounds as aminodiphenylether,

N-alkylaminodiphenylether,
N,N'-dialkylaminodiphenylether,
N,N,N'-trialkylaminodiphenylether,
N,N,N',N'-tetralkylaminodiphenylether,
aminodiphenylsulfide,
N-alkylaminodiphenylsulfide,
N,N'-dialkylaminodiphenylsulfide,
N,N,N'-trialkylaminodiphenylsulfide,
N,N,N',N'-tetralkylaminodiphenylsulfide,
aminodiphenylmethane,
N-alkylaminodphenylmethane,
N,N'-dialkylaminodiphenylmethane,
N,N,N'-trialkylaminodiphenylmethane,
N,N,N',N'-tetralkylaminodiphenylmethane,
aminodiphenylethane,
N-alkylaminodiphenylethane,
N,N'-dialkylaminodiphenylethane,
N,N',N'-trialkylaminodiphenylethane,
N,N,N',N'-tetralkylaminodiphenylethane,
aminodiphenylpropane,
N-alkylaminodiphenylpropane,
N,N'-dialkylaminodiphenylpropane,
N,N,N'-trialkylaminodiphenylpropane,
N,N,N',N'-tetralkylaminodiphenylpropane,
aminodiphenylbutane,
N-alkylaminodiphenylbutane,
N,N'-dialkylaminodiphenylbutane,
N,N,N'-trialkylaminodiphenylbutane,
N,N,N'N'-tetralkylaminodiphenylbutane, etc.

in which the alkyl group or groups contains from 1 to 20 or more carbon atoms each.

In still another embodiment the amine may comprise an alkanol amine including such compounds as ethanol amine, diethanol amine, propanol amine, dipropanol amine, butanol amine, dibutanol amine, pentanol amine, dipentanol amine, hexanol amine, dihexanol amine, etc., and N-alkylated and N,N-dialkylated alkanol amines in which the alkyl group or groups contain from 1 to 20 or more carbon atoms each. In still another embodiment the amine may comprise an aminophenol including, for example,

p-aminophenol,
o-aminophenol,
m-aminophenol,
2,6-dimethyl-p-aminophenol,
2,6-diethyl-p-aminophenol,
2,6-diisopropyl-p-aminophenol,
2,6-disecbutyl-p-aminophenol,
2,6-disecamyl-p-aminophenol,
2,6-disechexyl-p-aminophenol, etc.,
4-N,N-dimethylamino-2,6-diisopropylphenol,
4-N,N-dimethylamino-2,6-disecbutylphenol, etc.,
4-N,N-dimethylaminomethyl-2,6-diisopropylphenol,
4-N,N-dimethylaminomethyl-2,6-disecbutylphenol,
4-N,N-diethylaminomethyl-2,6-diisopropylphenol,
4-N,N-diethylaminomethyl-2,6-disecbutylphenol,
4-N,N-dipropylaminomethyl-2,6-diisopropylphenol,
4-N,N-dipropylaminomethyl-2,6-disecbutylphenol,
4-N,N-dibutylaminomethyl-2,6-diisopropylphenol,
4-N,N-dibutylaminomethyl-2,6-disecbutylphenol,
4-N,N-diethylaminoethyl-2,6-diisopropylphenol,
4-N,N-diethylaminoethyl-2,6-disecbutylphenol,
4-N,N-dipropylaminopropyl-2,6-diisopropylphenol,
4-N,N-dipropylaminopropyl-2,6-disecbutylphenol,
4-N,N-dibutylaminobutyl-2,6-diisopropylphenol,
4-N,N-dibutylaminobutyl-2,6-disecbutylphenol, etc.

It is understood that a mixture of amines may be employed and that the different amines are not necessarily equivalent, but all of them will serve to produce effective additives.

The additive of the present invention is prepared in any suitable manner. In a preferred method, the hydroxyhydrocarbon, including particularly alkylphenol or aliphatic alcohol, is oxyalkylenated by reacting with alkylene oxide, including particularly ethylene oxide, in the molar ratios to produce an oxyalkylenated hydroxyhydrocarbon containing the oxyalkylene group in the desired proportion. As hereinbefore set forth, in a preferred embodiment the additive contains from 2 to 12 oxyalkylene groups. More particularly, the number of oxyalkylene groups is from 2 to 6. The oxyalkylenation is effected in any suitable manner and generally will be conducted at a temperature of from about room temperature to about 350° F. and preferably from about 200° F. to about 300° F., preferably in the presence of a catalyst such as sodium hydroxide, potassium hydroxide, tertiary amine, quaternary hydroxide, etc. When the oxyalkylenation is to be limited to the addition of one oxy group, the catalyst may be omitted and the reaction is effected in the presence of water. Superatmospheric pressure may be employed, which may range from 10 to 1000 pounds or more.

The oxyalkylenated hydroxyhydrocarbon then is reacted in any suitable manner with P_2O_5 to form the desired phosphate. One molar proportion of P_2O_5 is reacted per one or two molar proportions of the oxyakylenated hydroxyhydrocarbon. In general, an excess of P_2O_5 is employed in order to insure complete reaction. The reaction is effected at a temperature ranging from room temperature to about 230° F. and under substantially anhydrous conditions. The resultant free acid form of the phosphate generally is recovered as a viscous liquid.

As hereinbefore set forth, the novel additive of the present invention is the amine salt. The amine salt is prepared in any suitable manner and is readily prepared by slowly adding the amine to the free acid form of the phosphate with intimate stirring. When the amine is a solid, it may be heated to melt the same. The reaction is effected at any suitable temperature, and preferably as low as practical. The temperature, therefore, preferably is within the range of from room temperature to 250° F. and more particularly to 150° F. In general, the neutral salt is preferred and is prepared by using equivalent amine and acid groups. Accordingly, this will depend upon whether a monoamine or polyamine is used and whether the mono- or di-(alkylenated hydroxyhydrocarbon phosphate) is used in preparing the salt. When the basic salt is desired, an excess of amine per acid group will be used and, when the acid salt is desired, a deficiency of amine per acid group is employed in forming the salt. Generally the amine salt will be recovered as a viscous liquid.

As hereinbefore set forth, the additive prepared in the above manner is incorporated in an oil of lubricating viscosity. In one embodiment the presence of water in the oil used for lubricating purposes should be minimized because water appears to have a detrimental effect on the lubricity properties of the additive. The additive possesses emulsifying properties and, therefore, will form an emulsion with water. However, in some cases, an emulsion of oil and water is used for lubrication purposes and, in such cases, the resultant emulsion will be used, with the understanding that the lubricity properties will be somewhat reduced. The same understanding applies when the oil of lubricating viscosity is used as a cutting oil, slushing oil, drawing oil, etc. However, in such cases, the lubricity properties may be sufficient to satisfy the particular requirements of such an emulsion.

While the additive of the present invention is readily soluble in most lubricating oils, particularly those containing aromatic hydrocarbons, the additive is not soluble to a desired degree in highly paraffinic oils and, in such cases, a solubilizing agent will be required to effect the desired solution of the additive in the oil.

The 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 hereinbefore set forth, when highly paraffinic lubricating oils are used, a solubilizing agent also is used.

The novel additive of the present invention is used in a small but stabilizing concentration in the oil of lubricating viscosity. Depending upon the particular use, the additive may be employed in a concentration of from about 0.01% to about 25% and preferably from about 0.5% to 10% by weight of the oil. When used in conventional lubricating oil, the additive generally may be 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 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 additive concentration is employed when the oil is used as transmission fluid, hydraulic fluid, industrial fluid, etc. When the oil is used in the formulation of a grease, the additive is used in a concentration of from about 0.5% to 5% by weight of the oil. When used in cutting oil, rolling oil, soluble oil, drawing compound, etc., the additive may be used in a concentration of from about 0.1% to about 10% by weight of the oil. When used in slushing oil, the additive may be used in a concentration of from about 0.1% to about 15% by weight or more of the oil.

It is understood that the additive of the present invention may be used along with other additives incorporated in the oil for specific purposes. In most cases, it is desirable to also incorporate an antioxidant in the oil. Preferred antioxidants are of the phenolic type and include tertiarybutylcatechol, 2,6-ditertiarybutyl-4-methylphenol, 2,4-dimethyl-6-tertiarybutylphenol, etc., 2-tertiarybutyl-4-methoxyphenol, 2-tertiarybutyl-4-ethoxyphenol, etc. Also, other additives incorporated in lubricating oil include metal deactivator, dye, viscosity index improver, pour point depressor, antifoaming additive, etc.

As hereinbefore set forth, the amine salt of the present invention is an emulsifying agent and, therefore, will serve to emulsify water and oil of lubricating viscosity for use as lubricating oil, slushing oil, cutting oil, rolling oil, soluble oil, drawing compound, etc. When desired, an additional emulsifying agent may be employed. Any suitable emulsifying agent can be used, including alkali metal sulfonates of petroleum sulfonic acids, mahogany sulfonates, naphthenic acids, fatty acids, etc., fatty alcohol sulfonates, pentaerythritol oleates, laurates, etc. The amount of water used in the emulsified oils will depend upon the particular use of the emulsion and may range from 0.25% to 50% or even up to 98% by weight of the composition.

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 additives of the present invention serve to stabilize the lubricity properties of the oil of lubricating viscosity, and the effectiveness of additives 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 disk and also 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 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, disk and pan are visually inspected immediately after the test to determine visible corrosion and also to determine whether deposit formation has occurred.

The oil of lubricating viscosity 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 of this example is the "Duomeen T" salt of polyoxyethylenated nonylphenol phosphate containing an average of about five oxyethylene groups. As hereinbefore set forth, "Duomeen T" is N-tallow-1,3-diaminopropane containing predominantly 16 to 18 carbon atoms in the alkyl group. The polyoxyethylenated nonylphenol phosphate is prepared in the manner hereinbefore described and the "Duomeen T" salt is prepared by heating the solid "Duomeen T" to a temperature of about 110° F. and adding 186 g. thereof gradually to 1000 g. of the polyoxyethylenated nonylphenol phosphate, with intimate stirring. The temperature is kept below that at which water is liberated in the reaction. The salt is formed using equivalent amine to acid groups.

The salt is recovered as a dark amber viscous oil having the following physical properties:

Specific gravity at 60° F.	1.0528
Viscosity:	
At 100° F., SUS	15,478
At 210° F., SUS	807.4
Flash point, COC, ° F.	470
Pour point, ° F.	25
Refractive index at 20° C.	1.49593

EXAMPLE II

The additive of this example is the salt of 2,5-dichloroaniline and the polyoxyethylenated nonylphenol phosphate, and was prepared by gradually adding 162 g. of 2,5-dichloroaniline to 1117 g. of the polyoxyethylenated nonylphenol phosphate, with intimate stirring. The resultant salt had the following physical properties:

Specific gravity at 60° F.	1.1257
Viscosity:	
At 100° F., SUS	8,196
At 210° F., SUS	255
Flash point, COC, ° F.	395
Pour point, ° F.	30
Refractive index, 20° C.	1.51228

EXAMPLE III

The additive of this example is the p,p'-N,N'-di-sec-butylaminodiphenylmethane neutral salt of the polyoxyethylenated nonylphenol phosphate. It was prepared by adding gradually 155 g. of p,p'-N,N'-di-sec-butylaminodiphenylmethane to 1117 g. of the polyoxyethylenated nonylphenol phosphate. The resultant salt had the following physical properties:

Specific gravity, 60° F.	1.0868
Viscosity:	
At 100° F., SUS	20,963
At 210° F., SUS	480.7
Flash point, COC, ° F.	415
Pour point, ° F.	30
Refractive index at 20° C.	1.50945

EXAMPLE IV

The additive of this example is the neutral salt of N,N'-bis-(1-methylheptyl)-ethylenediamine and polyoxyethylenated nonylphenol phosphate. The salt was prepared by gradually adding 144 g. of N,N'-bis-(1-methylheptyl)-ethylenediamine to 1117 g. of the polyoxyethylenated nonylphenol phosphate. The resultant salt had the following physical properties:

Specific gravity at 60° F.	1.0663
Viscosity:	
At 100° F., SUS	14,030
At 210° F., SUS	650.6
Flash point, ° F.	455
Pour point, ° F.	25
Refractive index at 60° F.	1.49602

EXAMPLE V

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). The table also reports the results of two separate runs made with different samples of the same oil, containing 1% by weight of two different preparations of the additive of Example I. These are shown in the table as Runs No. 2 and 3. Because the Carnes 340 White Oil is a paraffinic white oil, 1% of a solubilizing agent also was incorporated in the mixture in order to insure solution of the salt in the oil. The solubilizing agent, when evaluated in the same manner as described above, exhibited no potency in reducing the coefficient of friction and, accordingly, served solely as a solubilizing agent.

Table I

Run No.	Coefficient of Boundary Friction							Area of Wear Spot on Pin, mm.²			Deposit Formation
	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		0.102	0.635	0.532	Some.
2	0.09	0.11	0.11	0.10	0.09	0.09	0.05	0.159	0.219	0.060	None.
3	0.10	0.08	0.08	0.07	0.06	0.04	<0.04	0.126	0.219	0.093	None.

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

The results in Runs No. 2 and 3 utilizing the oil containing separate preparations of the "Duomeen T" salt of polyoxyethylenated nonylphenol phosphate showed 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 in Runs No. 2 and 3 was very low as compared to the 0.532 mm.² difference in the control run. Likewise, it will be noted that Runs No. 2 and 3 were free from deposit formation, whereas there was some deposit formed in Run No. 1.

EXAMPLE VI

As hereinbefore set forth, the amine salt should be used in the absence of water. Water appears detrimental and is demonstrated by the data in the following table. This run was made in the same manner as described in Example V, except that 1% by weight of water was included in the oil. The same additive of Example V was used in 1% by weight concentration in this run. For comparative purposes, Run No. 3 is repeated in the table.

Table II

Run No.	Water Present	Coefficient of Boundary Friction							Area of Wear Spot on Pin, mm.²			Deposit Formation
		72° F.	100° F.	150° F.	200° F.	250° F.	300° F.	350° F.	Original	Final	Difference	
3	No	0.10	0.08	0.08	0.07	0.06	0.04	<0.04	0.126	0.219	0.093	None.
4	Yes	0.11	0.14-S	0.14-S	0.15-S	0.05	0.05		0.219	0.528	0.309	Very little.

From the data in the above table it will be seen that the coefficients of friction at 100° F. to 200° F. were high and that seizure occurred. However, after the water had vaporized off, the coefficients of friction were satisfactory at 250° and 300° F. However, it will be noted that the wear spot on the pin was considerably higher in Run No. 4 than in Run No. 3, and that some deposit formation occurred in Run No. 4. Also, visual corrosion of the metal was noted in Run No. 4, but not in Run No. 3.

EXAMPLE VII

A number of different amine salts of the polyoxyethylenated nonylphenol phosphate was prepared and evaluated in the Carnes 340 White Oil in the same method as hereinbefore described. In all cases, the neutral salt was prepared and the additive was used in a concentration of 1% by weight of the oil.

The additive used in Run No. 5 is the rosin amine salt of the polyoxyethylenated nonylphenol phosphate. The rosin amine used in preparing the salt is marketed as "Rosin Amine D" by Hercules Powder Company.

The additive used in Run No. 6 is the 2,5-dichloroaniline salt of the polyoxyethylenated nonylphenol phosphate.

The additive used in Run No. 7 is the p,p'-diaminodiphenylmethane salt of the polyoxyethylenated nonylphenol phosphate.

The additive used in Run No. 8 is the p,p'-N,N'-di-sec-butylaminodiphenylmethane salt of the polyoxyethylenated nonylphenol phosphate as described in Example III.

The additive used in Run No. 9 is the N,N'-bis-(1-methylheptyl)-ethylenediamine salt of the polyoxyethylenated nonylphenol phosphate as described in Example IV.

The results of Runs No. 5 through 9 are reported in the following table.

Table III

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
5	0.13	0.12	0.13	0.12	0.12	0.11	0.09	0.055	0.219	0.169
6	0.10	0.10	0.09	0.09	0.08	0.08		0.321	0.528	0.307
7	0.09	0.10	0.10	0.10	0.09	0.09		0.102	0.219	0.117
8	0.10	0.09	0.09	0.09	0.09	0.09	0.08	0.102	0.321	0.219
9	0.12	0.11	0.11	0.10	0.10	0.09		0.159	0.410	0.251

Referring to the data in the above table, it will be noted that all of the amine salts were effective in stablizing the lubricity properties of the oil.

EXAMPLE VIII

As hereinbefore set forth, in addition to stabilizing the lubricity properties of the oil, it is desirable that the additive also serves as a corrosion inhibitor. The corrosion inhibiting properties of the additives of the present invention were evaluated in the Humidity Cabinet Method.

In this method, a highly polished steel panel is dipped into a viscous mineral oil, excess oil is drained, and the panel is placed in a humidity cabinet maintained at 120° F. in an atmosphere saturated with water. The panels are rotated slowly and the time required for visible corrosion to appear on the panel is reported.

The oil used in these tests is "Paraffin Oil No. 11" marketed by the American Oil Company. Typical specifications of this oil include the following:

Gravity, ° API	26.5–29.5
Viscosity:	
At 100° F., SUS	100–110
At 210° F., SUS	39.6
Flash point, COC, ° F.	350 min.
Pour point, ° F.	10 max.

The steel panel dipped in the above oil not containing an inhibitor undergoes visible corrosion in less than one hour. The following table reports results of evaluations made using different samples of the oil containing 1% by weight of the additives of the present invention.

Table IV

Sample No.	Additive of Run No.	Hours to Rusting
1	None	<1
2	2	23
3	3	23
4	5	23
5	7	47

From the data in the above table, it will be seen that the inhibitors reported above also were effective in reducing corrosion.

EXAMPLE IX

The additive of this example is the hydrogenated tallow amine salt of polyoxypropylenated tridecylalcohol phos-

phate. The additive is prepared by gradually adding, with intimate stirring, an equivalent of hydrogenated tallow amine to an equivalent of polyoxypropylenated tridecylalcohol phosphate containing 4 propylene oxide groups. Tridecylalcohol is oxypropylenated by reacting tridecylalcohol with propylene oxide, and the resultant polyoxypropylenated tridecylalcohol is reacted with P_2O_5 at a temperature of 160° F. to form the phosphate. The phosphate then is reacted with the hydrogenated tallow amine as described above.

The hydrogenated tallow amine salt of polyoxypropylenated tridecylalcohol phosphate as prepared in the above manner is used in a concentration of 2% by weight as an additive in transmission oil. The transmission oil is a solvent extracted lubricating oil having a viscosity of 150 SSU at 100° F. and 44 SSU at 200° F. (viscosity index 95).

EXAMPLE X

The additive of this example is the neutral salt of "Duomeen T" and polyoxyethylenated nonylphenol phosphate containing 3 oxyethylene groups. The salt is prepared by gradually adding an equivalent of "Duomeen T" to an equivalent of the polyoxyethylenated nonylphenol phosphate, with intimate stirring.

One percent by weight of the additive prepared in the above manner is added to an oil used commercially as a lubricant during the rolling of steel. The oil has an API gravity of 27.2°, a boiling range of about 566° to about 700° F. and a SUS viscosity at 100° F. of 58.9 seconds.

EXAMPLE XI

The additive of this example is the neutral "Duomeen T" salt of polyoxyethylenated dodecylphenol phosphate containing 8 oxyethylene groups. It is prepared in substantially the same manner as hereinbefore set forth.

The additive prepared in the above manner is used in a concentration of 2% by weight in a slushing oil composition containing 49% by weight of a lubricating oil having an API gravity of 24.5°, a pour point of −60° F., a flash point, COC, of 320° F. and a viscosity at 100° F. of 106 SUS, and 49% by weight of an aromatic naphtha having a boiling range of from about 200° to about 400° F. Steel panels are dipped into the slushing oil composition and thereby are protected against corrosion during subsequent storage and transportation of the steel panels.

EXAMPLE XII

The additive of Example I is used in a concentration of 2% by weight in di-(2-ethylhexyl) sebacate marketed under the trade name of "Plexol 201." This material is used as a synthetic lubricating oil and the incorporation of the additive therein serves to stabilize the lubricity properties of the lubricant during use under severe operating conditions.

EXAMPLE XIII

The neutral salt of "Duomeen T" and polyoxyethylenated nonylphenol phosphate containing 6 oxyethylene groups is used as an additive in soluble oils. Soluble oils vary from homogeneous compositions containing lubricating oil, soap and a small amount of water to emulsions of mineral oil and large amounts of water. These oils are used for cooling and lubricating in the cutting of metals. One percent by weight of the salt described above is incorporated in the soluble oil and serves to stabilize the lubricity properties thereof during use.

EXAMPLE XIV

One percent by weight of the neutral salt of "Duomeen T" and polyoxyethylenated nonylphenol containing 5 oxyethylene groups is used 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 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.

We claim as our invention:

1. Lubricating oil containing from about 0.01% to about 25% by weight of amine salt of polyoxyethylenated alkylphenol phosphate.

2. Lubricating oil containing from about 0.01% to about 25% by weight of diamine salt of polyoxyethylenated alkylphenol phosphate.

3. Lubricating oil containing from about 0.01% to about 25% by weight of the neutral salt of N-tallow 1,3-diaminopropane and polyoxyethylenated nonylphenol phosphate.

4. Lubricating oil containing from about 0.01% to about 25% by weight of an aniline salt of polyoxyethylenated nonylphenol phosphate.

5. Lubricating oil containing from about 0.01% to about 25% by weight of the 2,5-dichloroaniline salt of polyoxyethylenated nonylphenol phosphate.

6. Lubricating oil containing from about 0.01% to about 25% by weight of diaminodiphenylalkane neutral salt of polyoxyethylenated nonylphenol phosphate.

7. Lubricating oil containing from about 0.01% to about 25% by weight of the neutral salt, of N,N'-di-sec-butyl-aminodiphenylmethane and polyoxyethylenated nonylphenol phosphate.

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