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EXTREME PRESSURE LUBRICANT ADDITIVES

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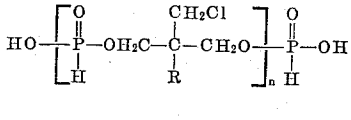
The present invention relates to novel functional fluid compositions, and more particularly to novel functional fluid compositions having improved load carrying characteristics. The invention is also directed to a novel method for increasing the load carrying properties of a broad spectrum of functional fluids.

It is well known that lubricating oils of themselves are often not able to protect metal surfaces and prevent metal to metal adhesion between contacting surfaces when the surfaces are subjected to extreme pressure. Under these circumstances, when bulk lubricant is forced from between the surfaces and the conditions of hydrodynamic lubrication cannot be maintained, the metal surfaces may "seize" or weld together. To increase the load carrying ability of lubricants, extreme pressure additives have been employed which create a protective film between the surfaces by reacting in some manner with the metal at the oil/metal interface. It has now been found the load carrying capacity of a broad spectrum of functional fluids of lubricating viscosity, including mineral oils, synthetic fluids and blends thereof, may be greatly enhanced by the addition of small amounts of a phosphorus containing polymer.

It has been demonstrated that certain phosphorus compounds have been able to produce moderate gains in the load carrying ability of selected lubricant blends. Phosphoric acid and organic phosphates have been heretofore employed in azelaic and sebacic acid diester fluids as well as in mineral oils. However, these compounds have shown only isolated areas of effectiveness, and were unable to fill the need for an effective extreme pressure additive for use throughout the broad spectrum of functional fluid compositions. For example, even in the area of dibasic acid diester fluids, superior load carrying characteristics have not been achieved with the economical adipic acid diester fluids by use of these phosphorus compounds as additives.

It is, therefore, an object of the present invention to provide an extreme pressure additive for use in a broad spectrum of functional fluids, which additive comprises a phosphorus-containing polymer obtained by reacting a trimethylol compound with phosphorus trichloride. It is a further object of this invention to provide a novel method for increasing the load carrying properties of a broad spectrum of functional fluids by adding to a functional fluid the extreme pressure additive of this invention. It is a still further object of this invention to provide novel functional fluid compositions having improved load carrying characteristics which comprise a mineral oil, a synthetic base fluid or a mixture thereof in combination with a small amount of an extreme pressure additive comprising said phosphorus-containing polymer. Further objects will become apparent in the light of the ensuing specification and claims.

In accordance with this invention, the load carrying ability of a broad spectrum of functional fluids may be increased by the addition of an extreme pressure additive of the formula



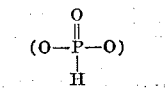
wherein R is a monovalent aliphatic radical, preferably a saturated aliphatic radical comprising carbon and hydrogen and free from additional atoms other than chlorine and oxygen in the form of hydroxyl groups, ester linkages, ether linkages and keto linkages. Illustrative radicals include alkyl, such as methyl, ethyl, propyl, 2-methyl propyl, butyl, t-butyl, hexyl, octyl, decyl, isodecyl, dodecyl, hexadecyl eicosyl and the like; chloroalkyl such as chloromethyl, 2-chloroethyl, 3-chlorobutyl, 6-chlorohexyl, 10-chlorodecyl, 9-chlorododecyl and the like; alkoxyalkyl such as ethoxyethyl, methoxyethyl, ethoxymethyl, methoxypropyl, ethoxyhexyl, butoxydecyl, butoxyhexadecyl, and the like; chloroalkoxyalkyl such as chloroethoxyethyl, chloromethoxypropyl, 4-chlorobutoxydodecyl and the like; alkanoylalkyl such as acetylethyl, butanoylhexyl ethanoyldecyl and the like, and chlorinated derivatives thereof such as chloroacetylethyl, acetyl-3-chlorobutyl and the like; and alkanoyloxyalkyl such as acetyloxyethoxy, butanoyloxyhexyl and the chlorinated derivatives thereof such as chloroacetyloxyethyl and the like. Preferred organic radicals are chloroalkyl and alkyl, the latter being highly preferred. Particularly contemplated are those compounds wherein the said R substituents contain from 1 to 20 carbon atoms. Highly preferred radicals have to 1 to 12 carbon atoms.

The phosphorus polymers which are useful as extreme pressure additives in the novel functional fluids of the instant invention generally possesses an average molecular weight in the low or intermediate range. Typically the phosphorus polymers employed in the novel functional fluids of this invention contain an average of from 2 to about 12 of the repeating units structurally described. Although polymers of longer chain length are not lacking in beneficial extreme pressure properties, and such longer chain polymers may be employed consistent with their solubility in the base fluid in which they are employed. The longer chain polymers have been found to be more insoluble in general, although solubility may be suitably adjusted by proper selection of the R substituent or by use of a solvent as hereinafter provided. Most commonly employed are polymers having an average chain length of from 4 to 8 repeating units. The molecular weight of the polymer, which is concurrently dependent on both the number of repeating units and the size of the R substituent, may vary from about 400 to about 12,000.

In general, the nature and size of the R substituent in the extreme pressure additives of this invention may be varied in accordance with considerations of stability and solubility of the extreme pressure additive at the conditions under which the ultimate formulations are to be employed. Where it is anticipated that the ultimate formulations are to be used at elevated temperatures, the organic moiety designated by R is preferably free from functional groups which are readily oxidizable or which are thermally unstable at such elevated temperatures. Accordingly, for ultimate formulations for use at elevated temperatures, the R moiety of the extreme pressure additive is more desirably alkyl or chloroalkyl. Where the ultimate compositions are intended for use under conditions where thermal stability is not paramount, the principal considerations dictating the nature of the organic moieties of the extreme pressure additives is the effect of said moieties on the solubility of the polymer in the base fluid.

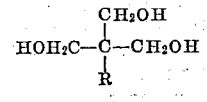
Accordingly, variations in the R substituent can be made in contemplation of facilitating the solubility of the polymer in the base fluid in which it will be employed. In general, in ester-type base fluids and the like, which have a large weight percentage of polar groups, such as the carbonyloxy linkage, the oxy linkage, the carboxylic

acid group or the hydroxyl group, it is more desirable to employ phosphorus-containing extreme pressure additives wherein the organic moieties designated by R, above, are such that the resulting repeating units of the polymer are of low molecular weight. This will result in the extreme pressure additive possessing a large percentage of phosphite linkages, i.e.,



per unit of molecular weight, and thus render the polymer more soluble in the fluid. On the other hand in hydrocarbon fluids or mineral oils where the percentage of polar linkages in the base fluid is smaller and, thus the molecular ratio of hydrocarbon linkages is greater, the molecular weight of the R substituent in the phosphorus containing polymer, above, is advantageously increased, rendering the polymer more soluble in this type of fluid.

The phosphorus-containing polymers employed as extreme pressure additives in accordance with the instant invention can be prepared by contacting phosphorus trichloride and a trimethylol compound of the formula:



wherein R is as hereinbefore described.

The phosphorus containing polymers are obtained by contacting the aforementioned reactants at a temperature at which the trimethylol compound is liquid and removing the hydrogen chloride formed as a gas. This temperature will generally be above room temperature and preferably in the range of from about 40° to about 135° C. although higher temperatures, e.g., 150° and 175° C. may be employed. At lower temperatures the reaction mixture tends to thicken. It has been found preferable to employ temperatures above the boiling point of phosphorus trichloride to hasten the reaction. It is especially preferred to operate at a temperature of from about 100° C. to about 115° C. The ensuing reaction results in a product mixture which contains the phosphorus-containing polymer.

In accordance with this invention, there are provided novel functional fluid compositions comprising a functional base fluid of lubricating viscosity and a small amount, sufficient to increase the load carrying ability of the fluid, of an extreme pressure additive as hereinbefore described. Likewise there is provided a novel method for increasing the load carrying ability of a functional base fluid which comprises adding the aforesaid extreme pressure additive thereto in such small amount. It is pointed out that the phosphorus containing polymer can be employed as an extreme pressure additive either as the crude reaction product mixture obtained from the above reaction, or in a refined, concentrated state obtained by further treatment of the crude reaction product mixture.

In order to obtain the extreme pressure additive in the refined concentrated state, the crude reaction product mixture obtained from the above reaction is subjected to vacuum stripping. This stripping is conducted in a distillation apparatus at progressively increasing pot temperatures and progressively decreasing pressures until a still residue of essentially constant weight is obtained. The pot residue is substantially composed of the phosphorus containing polymer hereinbefore described. The overhead from the stripping operation contains unreacted trimethylol compound as well as organic phosphorus by-products of the reaction. These organic phosphorus by-products of the reaction are believed to possess load carrying ability themselves, particularly when used in the reaction product mixture. However, it is postulated that

the phosphorus polymer is the major load carrying ingredient.

In the conduct of the stripping operation, pressures are generally reduced below 10 millimeters of mercury, and pressures as low as 0.1 millimeters of mercury can be employed. Reduced pressures of about 0.5 to 2.0 millimeters of mercury are usually sufficient. The pot temperature during the distillation should in general not be permitted to rise to within less than about 25° C. of the decomposition temperature of phosphorus containing polymer. Advantageously, the temperature is not permitted to exceed 200° C.

For purposes of reference, hereinafter the extreme pressure additives shall be referred to as consisting of the phosphorus-containing polymer in the concentrated state, or in the reaction product state. The former designation refers to the phosphorus-containing polymer after it has been separated from the crude reaction product mixture by the stripping operation as hereinbefore set forth. The latter term is meant to refer to the crude reaction product mixture itself, which may also be employed without further purification, as an extreme pressure additive.

The ultimate novel functional fluid compositions of this invention comprise a major amount of a functional base fluid of lubricating viscosity and a small amount of the phosphorus-containing polymer sufficient to impart improved extreme pressure properties to the fluid. Preferably from about 0.005 to about 10 percent by weight, based on the fluid, of the phosphorus-containing polymer is employed. About 0.1 to about 2 percent by weight of the polymer is highly preferred. As hereinbefore disclosed the polymer may be employed in the refined concentrated state or as the crude reaction product mixture. Inasmuch as the latter contains phosphorus by-products which appear to also contribute to the load carrying ability of the fluid it has been found that small amounts of either the concentrated polymer or of the crude reaction product mixture, in the above amounts are highly satisfactory.

As hereinbefore stated the extreme pressure additives of the present invention are useful in a broad spectrum of functional fluids including lubricants such as those for automotive or aircraft use, and gear and bearing lubricants, industrial fluids such as metal working fluids, power transmission fluids such as those used in automobile transmissions, hydraulic fluids and the like, the use of which fluids is dependent at least in part upon the lubricating property of the fluid. The phosphorus-containing polymers may be employed in mineral oils or in a broad range of synthetic functional fluids or in blends of said mineral oils and said synthetic fluids. The base fluids contemplated for use with the extreme pressure additives of the invention are generally those whose contemplated use demands some lubricity characteristics. The viscosities of the base fluids may extend from those of light oils to those base fluids of grease consistency.

The novel functional fluids are prepared by admixing the functional base fluid and the extreme pressure additive in the concentrated state or in the reaction product state. The mixing is preferably carried out at elevated temperatures, i.e., about 60° C. to 150° C. or higher. However, solubility difficulties may be encountered particularly when the extreme pressure additives are to be employed in adipic acid diester fluids. To aid in solubility of the extreme pressure additive, in the concentrated state or in the crude reaction product state, it is premixed with an alcoholic hydroxy compound. The term alcoholic hydroxy compound, as used herein, refers to any compound containing a truly alcoholic hydroxyl group, i.e., a hydroxyl group contiguously linked to a saturated carbon atom, and which also is free of other groups which might react with the polymer. Generally preferred are alcoholic hydroxy compounds which consist essentially of carbon and hydrogen, with oxygen in

the form of oxy linkages, carbonyloxy linkages, carbonyl groups, and, of course, hydroxy groups. The alcoholic hydroxy compounds may contain 1 or a plurality of hydroxyl groups such as alkane diols, alkane triols and like hydrocarbon alcohols having from 4 to 36 carbon atoms. The alcoholic hydroxy compounds are not meant to include compounds which are dissimilar from alcohols such as reducing sugars, hydrates of carbonyl compounds, e.g., formaldehyde hydrate. The alcoholic hydroxy compound is combined with the phosphorus-containing polymer in the concentrated or reaction product state, in an amount sufficient to enable the polymer to become soluble in the base fluid. This premixing with hydroxy compound is generally accomplished by moderately heating the polymer to about 100° to 125° C. with one or a mixture of said alcoholic hydroxy compounds in a ratio within the range of from about 2 to 95 parts of the phosphorus-containing polymer to about 98 to 5 parts of the alcoholic hydroxy compound. Most commonly about 50 to 95 parts of the polymer are premixed with 5 to 50 parts of the alcoholic hydroxy compound to attain desirable solubility characteristics.

Suitable hydroxyl containing compounds which may be premixed with the extreme pressure additives of the invention include the aliphatic alcohols, particularly the C_4 to C_{24} alkane alcohols, such as butanol, pentanol, 4-methyl-2-pentanol, 2-methylpentanol, 2-ethylhexanol, 2,6,8-trimethylnonanol, isodecanol, lauryl alcohol, oleyl alcohol, tridecanol, tetradecanol, pentadecanol, hexadecanol, octadecanol, and the like; the alkyl glycols such as ethylene glycol, propylene glycol, propane-1,3-diol, butane-1,3-diol, butane-1,4-diol, 2-methyl-1,3-pentanediol, 2,2,4-trimethylpentane-1,3-diol, pentane-1,5-diol, 2-ethylhexane-1,3-diol, 2-methyl-2-ethylpropane-1,3-diol, hexane-1,3,6-triol, and the like; the polyalkylene glycols such as polyethylene glycol, polypropylene glycol, polybutylene glycol, mixed polyalkylene glycols such as those prepared from physical mixtures of oxides, for example mixed oxyethylene-oxypropylene glycol, and the like; monoalkyl ethers of the above glycols and polyalkylene glycols such as diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, ethylene glycol monohexyl ether, 1-butoxyethoxy-2-propanol, propylene glycol monomethyl ether, dipropylene glycol monomethyl polypropylene glycol monoethyl ether, mixed oxyethylene oxypropylene glycol monobutyl ether and the like; the monoalkyl esters of glycols or polyalkylene glycols prepared by reacting them with an aliphatic dibasic acid such as adipic azelaic, pimelic, sebacic acid and the like; and aliphatic hydroxy acids such as glycolic acid, lactic acid, 3-hydroxybutyric acid, 4-hydroxymethylpentanoic, and ricinoleic acid and the like.

Since phosphoric acid is a well known catalyst for the dehydration of alcohols, the mixing of the phosphorus-containing polymer in either the concentrated state or the reaction product state and the hydroxy compounds may result in some dehydration of the latter to an alkene. Alcohols vary in the ease with which they will undergo such dehydration. In general, it may be stated that alcohols of highly branched-chain structure are particularly susceptible. Tertiary alcohols are dehydrated most easily, secondary are next, and primary alcohols are least easily converted to alkenes. Thus the dehydration may take place to a greater or lesser extent, or not at all, depending upon the hydroxy compound employed. When such dehydration occurs the resulting mixture of the phosphorus containing polymer and the hydroxy compound separates in two phases. The upper, less dense phase, which has no load carrying properties, contains those dehydration products formed from the hydroxy compound. This upper layer is then desirably separated by distillation or similar conventional means from the lower layer. The load carrying properties of the phosphorus-containing polymer dissolved in the lower, more dense layer are not adversely affected by the dehydration.

The functional base fluids in which the extreme pressure additives of the instant invention may be employed traverses the broad spectrum of functional fluids including mineral oils, synthetic fluids, and mixtures of the two, as well as in greases derived therefrom.

The functional base fluid with which the phosphorus-containing polymeric extreme pressure additives is admixed is preferably a lubricant base fluid of the type otherwise best suited for the particular use for which the ultimate formulation is designed. Accordingly, a single oil or synthetic oily derivative of the desired characteristics, or a blend of oils of lubricating viscosity may be employed as the lubricating base fluid by means of which any desired characteristics, e.g., viscosity, can be obtained. The base fluids can contain one, or a combination of fluids such as mineral oils, synthetic oleaginous simple esters, as well as di- and poly-esters, complex polymeric esters, polyoxyalkylene glycols, ethers and esters, thereof prepared from alcohols, acids and alkylene oxides, polymers, formals, polyformals and the like.

Among the useful functional base fluids which are advantangeously employed with the extreme pressure additives of this invention are mineral base oils manufactured by fractionation of crude oils. Subsequent refinement of these oils can be accomplished by dewaxing with acid and solvent, and clay treatment. Suitable mineral base oils may be of the pure paraffin type, the mid-continent or semi-paraffin type, or of the naphthene type. The extreme pressure additives of the invention may also be advantageously employed in greases, consisting of a mineral oil that has been thickened by compounding with a soap such as lithium hydroxy stearate and the like, and an inorganic thickener.

The synthetic base fluids which are useful in conjunction with the extreme pressure additives of the present invention include, among others, simple diesters prepared from dicarboxylic acids fully esterified with monohydric alcohols. The total number of carbon atoms in the diester molecule is about 20 to 36, preferably 22 to 26. Preferred dicarboxylic diesters are those of the formula:

$$R_1OOCR'COOR_1$$

wherein each R_1 may be the same or different, and represents the hydrocarbyl portion of a monohydric alcohol and can be a straight or branched chain alkyl radical of an alkanol having about 6 to 13 carbon atoms or cycloalkyl radical of a cycloalkanol having 5 to 7 ring carbon atoms, wherein R' is a straight or branched chain divalent aliphatic hydrocarbon radical containing from 2 to 8 carbon atoms preferably saturated, or the phenylene or naphthalene radical. Examples of such include: di(2-ethylhexyl) sebacate, di(2-ethylhexyl)azelate, di[mixed-(2-ethylhexyl, isodecyl)] azelate, di(2-ethylhexyl)adipate, di(isooctyl) adipate, di(undecyl) adipate, di(tetradecyl) adipate, di(heptadecyl) adipate, di(2,2,4-trimethylpentyl) adipate, di(1-methylcyclohexylmethyl) adipate, di(1-ethylpropyl) azelate, di(3-methylbutyl)azelate, di(2-ethylbutyl) azelate, di(1-ethylpropyl) sebacate, di(3-methylbutyl)sebacate, di(1,3-dimethylbutyl) sebacate, di(2-ethylbutyl) sebacate, di(2-[2'-ethylbutoxy]ethyl) sebacate, di(undecyl) sebacate, di(tetradecyl)sebacate, di (heptadecyl)sebacate, di(n-nonyl)adipate, di(C_8 - Oxo) azelate, di-n-heptyl isosebacate, di(C_{10}-Oxo) adipate, di (C_8-Oxo) adipate, di(C_7-Oxo) adipate, di(C_8-Oxo) trimethyl adipate, di(C_8-Oxo) sebacate, di(C_9-Oxo) sebacate, di(C_{13}-Oxo) sebacate, di(C_{13}-Oxo) pimelate, diethyl phthalate, di-n-butyl phthalate, di(isoamyl) succinate, di(n-butyl) tartrate, di(2-ethylhexyl) maleate, triamyl citrate, di(methylcyclohexyl) adipate, di(2-ethylhexyl) azelate, di(3,5,5-trimethylhexyl) sebacate, dicapryl sebacate, dimethylglycol phthalate, di(2-butoxyethyl) azelate, di(1-methyl-4-ethyloctyl) adipate, di(3-methylbutyl) adipate, di(2-ethylhexyl) adipate, di(3,5,5-trimethylhexyl) adipate, di(methylcyclohexyl) adipate,

di(2-butoxyethyl)azelate, di(methylcyclohexyl) pimelate and the like.

Different esters can, of course, be selected according to the conditions under which the novel functional fluids are to be used. For example, esters of high molecular weight, and particularly the higher, branched chain diesters of adipic, azelaic and sebacic acid are preferred in compositions for use at very high temperatures, i.e., temperatures in the neighborhood of about 350° F. The esters of adipic acid have the additional advantage of being considerably cheaper than the esters of the azelaic and sebacic acids.

Polybasic acids useful for preparing the esters include, among others, phthalic, succinic, maleic, malic, tartaric, pyrotartaric, glutaric, adipic, pimelic, suberic, azelaic, sebacic and pinic acids. Useful alcohols which may be employed in esterifying the polybasic acids are 2-ethylhexyl alcohol, isooctyl alcohol, isodecyl alcohol, 2-ethylbutyl alcohol, cetyl alcohol, n-octyl alcohol, amyl alcohol, oleyl alcohol, 2-butyloctyl alcohol, methyl and dimethyl cyclohexanol, and the "Oxo" alcohols. Diesters prepared from the Oxo alcohols, which are isomeric mixtures of branched chain alkanols, are particularly desirable. The Oxo alcohols have a very high degree of branching in the hydrocarbon chain, which results in diester oils having low pour points and low viscosity at low temperature. These alcohols are prepared from olefins, such as polymers and copolymers of C_3 and C_4 monoolefins, which are reacted with carbon monoxide and hydrogen in the presence of a cobalt-containing catalyst such as a cobalt carbonyl catalyst, at temperatures of about 300° to 400° F., and under pressures of about 1000 to 3000 p.s.i. to form aldehydes. The resulting aldehyde product is then hydrogenated to form the Oxo alcohol which is then recovered from the hydrogenation product. Other operable diesters are those prepared from glycols and monocarboxylic acids such as dipropylene glycol dipelargonate, polyethylene glycol dicaproate, and the like.

Other suitable base fluids include polyesters such as those prepared by reacting polyhydric alcohols such as trimethylolalkanes, e.g., 1,1,1-trimethylolpropane, 1,1,1-trimethylolethane and pentaerythritol with monocarboxylic acids such as butyric acid, caproic acid, caprylic acid, pelargonic acid, and the like, to give the corresponding tri- or tetraesters.

Useful complex esters which may be used as the base lubricating fluid include those formed by esterification reactions between a dicarboxylic acid, a glycol, and an alcohol and/or a mono-carboxylic acid. These esters may be represented by the following formulas:

$$R_2COO—R_4—(OOCR_3COO—R_7)_n—OOCR_2$$

$$R_2—OOCR_3COO—(R_4—OOCR_5COO)_n—R_6$$

$$R_2(OOCR_3COO—R_4)_n—OOCR_6$$

wherein R_2 and R_6 are alkyl radicals of a monohydric alcohol (e.g. alkanols), or a monocarboxylic acid (e.g. alkanoic acids), R_3 and R_5 are hydrocarbon radicals of dicarboxylic acids (e.g. alkandioic acids), and R_4 and R_7 are divalent hydrocarbon or hydrocarbyloxy radicals, such as $—CH_2(CH_2)_n—$ or

$$—CH_2CH_2(OCH_2CH_2)_n—$$

or $CH_2CH(CH_3)OCH_2CH(CH_3)—$, derived from an alkylene glycol or polyalkylene glycol; "*n*" in the complex ester molecule, will usually range from 1 to 6 and is controlled by the relative molar ratio of the glycol or polyglycol to the dicarboxylic acid. In preparing the complex ester, there will always be some simple ester formed, i.e. $n=0$, but this will generally be a minor portion.

Some specific materials used in preparing the above types of complex esters are alkanols having 6 to 13 carbon atoms such as n-butyl alcohol, 2-ethylbutyl alcohol, 2-ethylhexanol, n-hexyl alcohol, C_8 Oxo alcohol and C_{13} Oxo alcohol, etc.; the corresponding fatty or monocarboxylic acids; dicarboxylic acids and C_2 to C_8 glycols such as ethylene glycol, propylene glycol, pentane-1,5-diol, 2-ethylhexane-1,3-diol and the like. In addition the corresponding thioglycols may be used, e.g. β,β'-dihydroxyethyl sulfide. In general these complex esters will have a total of 20 to 80, preferably 30 to 50, carbon atoms. These complex esters and methods for their preparation are known in the art.

Other useful complex polyesters include those prepared by direct esterification of dibasic acids with glycols or by transesterification of lower alkyl di-esters of dibasic acids by reacting about equimolar amounts of a dibasic acid or a dibasic acid diester with a glycol, in the case of the diester said glycol having a boiling point higher than the alcohol used to prepare the diester. The reaction is conducted at 300° F. or higher for a period of time sufficient to complete the ester interchange to obtain a product having lubricating viscosity, preferably a kinematic viscosity from about 40 to 200 centistokes at 210° F. Suitable dibasic acids include the C_2 to C_{28} alkane and alkene dioic acids and preferably those of not more than 12 carbons. Such acids include succinic, adipic, suberic, azelic, sebacic and "isosebacic" acids which are mixtures of alpha-ethyl suberic acid, alpha,alpha'-diethyl adipic acid, brassic, brassylic, pentadecandicarboxylic acid, tetraicosanedicarboxylic acid, C_4 to C_{24} alkenylsuccinic acids, diglycolic acid, and thiodiglycolic acid. Useful glycols include alkane diols of 3 to 12 carbon atoms but more preferably polyoxyalkylene glycols having up to 50 ether oxygen linkages. Preferred polyglycols are the polypropylene glycols particularly those having molecular weights from about 100 to 4000. The preferred ratio of acid to glycol is about 1:1. If desired, the reaction can be accelerated by employing an esterification catalyst such as, e.g., paratoluene sulfonic acid. The temperature of the reaction mixture is advantageously maintained sufficient to drive off the water formed in the reaction but not so high as to decompose the desired product. In general, temperatures from about 350 to 400° F. are satisfactory.

Other suitable fluids are esters of aromatic acids which correspond to the general formula:

$$Z(COOR_1)_n$$

wherein *n* is an integer from 2 to 4, Z is a benzene or naphthylene nucleus substituted to the degree indicated by *n*, the remaining substitution being hydrogen substitution, and each R has the same meaning as previously described above in regard to the dibasic acid esters.

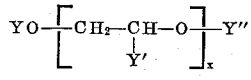
Examples of acids from which the aromatic esters can be prepared include, phthalic, terephthalic, pyromellitic and naphthalene-1,4-dicarboxylic acid. Inasmuch as the R substituent is commensurate in scope, the alcohols which are reacted with the aromatic acids are the same as those mentioned with regard to the dibasic acid esters above.

Dibasic acid esters are extremely useful as aircraft lubricants particularly for turbojet and turboprop applications. Aliphatic diesters have superior viscosity properties over a wide temperature range making them useful in aircraft engines. In applications where high film strength is called for, higher molecular weight complex esters, made by linking dibasic acids through a polyglycol center, are uniquely suitable. Blends of complex esters and dibasic acid esters have been used to formulate base fluids for gas turbine engines. Although the predominant use of dibasic acid esters is in jet lubricants, outlets for these synthetics in low temperature greases, gear oils, instrument oils and hydraulic fluids are growing.

With regard to dibasic acid esters, general structural considerations suggest that low temperature viscosity would be favored by short branches from the main diester chain. Increasing chain length increase viscosity, improves viscosity temperature characteristics, and raises

freezing point. The addition of side chains increases viscosity, lowers pour point and may impair the viscosity index depending upon the number and size of the branches. The addition of cyclic groups causes larger incerases in viscosity and larger decreases in viscosity index than aliphatic chains.

The extreme pressure additives of the instant invention are also admirably suitable for use in polyglycols. The class of compounds commonly referred to as polyglycols encompasses the essentially linear polymers consisting of carbon, hydrogen, and oxygen having the generalized formula:



wherein Y, Y′ and Y″ are monovalent organic radicals selected from the group of hydrogen, and monovalent organic radicals such as aliphatic groups, aryl groups, or acyl groups, and more particularly wherein Y′ is selected from the group consisting of hydrogen and alkyl and Y and Y″ are selected from the group consisting of hydrogen, alkyl, and alkanoyl groups and wherein Y′ can be varied to provide homopolymers or heteropolymers. This class of compounds include polyalkylene glycols, particularly polyethylene glycol and polypropylene glycol, as well as mixed oxyethylene-oxypropylene glycol, the mono-alkyl ethers of polyalkylene glycols, such as polyethylene glycol monomethyl ethers, polypropylene glycol monobutyl ethers, the monooctyl ethers of mixed oxyethylene-oxypropylene glycol and the like, dialkyl ethers of the polyalkylene glycols such as the dimethyl ethers of polyethylene glycol, and the ethyl ethers of butoxy-polypropylene glycol, the ether-esters of polyalkylene glycols such as the phenyl ethers of polypropylene glycol acetate, butyl ethers of polyethylene glycol maleate, and the like, or diesters of the polyalkylene glycols such as di-2-ethylhexanoate of mixed oxyethylene-oxypropylene glycol.

This class of compounds, as well as methods for the preparation of individual members can be found in U.S. Patents Nos. 2,293,868; 2,425,755; 2,425,845; 2,448,664; 2,520,611 and 2,520,612.

These polyglycol lubricants, when properly inhibited, are relatively stable to oxidation at temperatures as high as 450° F. They are used as journal bearing lubricants, gear lubricants, carrier oils for graphite or molybdenum disulfide, internal combustion engine lubricants and the like. They also find use as metal working fluids, automotive brake fluids and in the manufacture of fire resistant hydraulic fluids. Polyglycols have also been used in greases in specialty applications where some advantageous property of the glycol is utilized. Lithium soap combinations with polyglycols have yielded greases with good properties. In all the above applications the phosphorus containing polymers of the instant invention may be advantageously employed where extreme pressure conditions are contemplated.

In the formulation of finished lubricant compositions proportion of the simple esters, polyesters, polyoxyalkylene glycols and other synthetic components and mineral oils in the base lubricating fluids can vary over a wide range and will depend upon the desired utility of the ultimate formulation and the characteristics required therefor. The above components are preferably compounded to yield base fluids of the type otherwise best suited for the particular use for which the ultimate formulations are designed. Thus, where the finished formulation is intended for use at elevated temperatures, it is advantageous to employ a lubricating base fluid which is thermally stable at the contemplated lubricating temperatures. Some mineral oils, especially "hydro-fined" mineral oils, when employed in the lubricant base fluids of the present novel functional fluid formulations, are sufficiently stable to be used under moderately elevated temperatures. Where temperatures in the order of 400° F. or above are to be encountered, the base fluid is preferably compounded from the synthetic oily esters or polymers.

In accordance with this invention, there are provided novel lubricant compositions comprising mono-alkyl ethers of polyoxyalkylene glycols, dialkyl ethers of polypropylene glycols, or mixtures thereof, having the thermal and oxidative stability, viscometric behavior, satisfactory volatility and hydrodynamic lubricating characteristics necessary for functional fluid application, such as in automotive transmissions (automatic and nonautomatic) hypoid differentials, hydraulic pumps, and the like. These fluids are adaptable for use in both transmissions and axle differential gear boxes, and single unit automatic transmission-differential (transaxle systems).

In another specific aspect there is provided lubricant compositions compounded from petroleum oils, dialkyl ethers of polyoxyalkylene glycols and alkandioic acid diesters which have the necessary thermal and oxidative stability, viscometric behavior, resistance to shear breakdown, satisfactory volatility and hydrodynamic lubricating characteristics suitable for use in both transmissions and axle differential gear boxes and in single unit automatic transmission differential (transaxle) systems.

In accordance with this invention the extreme pressure additives may be employed in a broad spectrum of base fluids having a wide variety of end uses. For example, a lubricant meeting all requirements as a transaxle fluid may be composed of a mixture of polyglycols such as polypropylene glycol monobutyl ether and the ethoxy monobutyl ether of polypropylene glycol. Other useful transaxle lubricants may be comprised of such glycols and up to 50 percent by weight of a dibasic acid diester. Novel rock drill lubricants for use at low temperatures may be formulated using the extreme pressure additives of this invention in a comparatively low molecular weight polyglycol such as a monoalkyl ether of polypropylene glycol having a molecular weight, i.e. about 500 to about 800.

Useful aircraft lubricants may be formulated utilizing the extreme pressure additives with dibasic acid esters or with diester-polyglycol blends. Such blended compositions preferably may contain from about 25 to 95 percent of the diesters and from 5 to 75 percent of a polyglycol monoether.

Finished lubricant compositions containing the extreme pressure additives of the instant invention normally contain other well known additives which act as antioxidants, corrosion inhibitors, metal deactivators, viscosity index improvers, dispersancy agents and the like. Effective antioxidants include the amine and the phenolic types of antioxidants such as N-phenyl-α-naphthylamine and 2,6-ditertiarylbutyl - 4 - methylphenol. Although the extreme pressure additives of this invention exhibit anti-corrosion properties, it may be desirable to augment corrosion protection by incorporation of corrosion inhibitors such as the nitrogen-containing heterocyclics, i.e., benzoguanamine, cyanuric acid, and benzimidazole. Exemplary metal deactivators include sulfur containing compounds such as mercaptobenzothiazole. Polymerized wax-alkylated naphthalenes and phenols, polyalkyl acrylates and poly (alkyl)methacrylates are advantageously employed as pour point depressants. Phosphate esters such as tricresyl phosphate act as effective anti-wear additives. Silicone fluids are useful also for this purpose, and in addition act as anti-foamants when used at extremely low concentrations. Viscosity index improvers are polymeric materials including polyisobutylenes, alkylated polystyrene, polyacrylates and polymethacrylates.

In producing the extreme pressure additives of this invention, trichloride is added slowly to the trimethylol compound with mixing. Inasmuch as the addition of the phosphorus trichloride is accompanied by an exotherm, it is desirable to control the temperature of the reaction either by measured addition of phosphorus trichloride or by use of external cooling means. Such measured addi-

tion is preferred, since the formation of the polymer is favored by the presence of a slight excess of the trimethylol compound, and rapid addition of the phosphorus trichloride would produce a localized molar excess of this compound. In general, it is desirable to keep the temperature as low as possible, thus temperature is preferably not permitted to ascend more than 25° C. in excess of the temperature required to maintain the trimethylol compound as a liquid. The compounds are preferably reacted in such molar quantities as to favor formation of the polymer, i.e., the trimethylol compound is maintained in slight excess. Simultaneously with the addition of phosphorus trichloride, a dry inert gas, e.g., nitrogen is passed through the reaction mixture to carry off the hydrogen chloride by-product of the reaction. The reaction is preferably conducted under essentially anhydrous conditions since phosphorus trichloride will readily react with water to produce hydrogen chloride gas. For this reason, also, it is preferred that the addition of the phosphorus trichloride to the trimethylol compound be accomplished in an inert atmosphere or in such other manner as to avoid contact with atmospheric moisture, since such contact will result in hydrogen chloride evolution. Upon completion of the addition of phosphorus trichloride, the reaction mixture is advantageously maintained at a temperature of about 100° to 125° C. with a continuous purge of inert gas until hydrogen chloride evolution has essentially ceased. The removal of hydrogen chloride may be desirably facilitated by reducing pressure to about 5 to 10 millimeters of mercury while continuing to sweep the reaction product mixture with inert gas.

Useful trimethylol compounds for preparing the phosphorus containing extreme pressure additives include 1,1,1-trimethylol alkanes such as 1,1,1-trimethylol ethane, 1,1,1-trimethylol propane, 1,1,1-trimethyol heptane, 1,1,1-trimethylol-2-ethylhexane, 1,1,1-trimethylol hexadecane and the like, the 1,1,1-trimethylol chloroalkanes such as 1,1,1-trimethylol-2-chloroethane, 1,1,1-trimethylol-3-chloropropane, 1,1,1-trimethylol-3-chlorobutae, 1,1,1-trimethylol-6-chlorohexane and the like, the 1,1,1-trimethylol-alkoxy alkanes, such as 1,1,1-trimethylol methoxypropane, 1,1,1-trimethylol methoxyhexane, 1,1,1-trimethylol ethoxybutane, 1,1,1-trimethylol butoxyhexane and the like as well as the chlorine substituted derivatives of said 1,1,1-trimethylol alkoxyalkanes such as 1,1,1-trimethylol methoxy-2-chloroethane and the like, the 1,1,1-trimethylol alkanoylalkanes such as, 1,1,1-trimethylol acetylethane, 1,1,1-trimethylol acetylpropane, 1,1,1-trimethylol propanoylbutane and the like including the chlorine substituted derivatives of said 1,1,1-trimethylol alkanoyl-alkanes such as 1,1,1-trimethylol, acetyl-2-chloroethane and the like. Preferred are trimethylol ethane, trimethylol propane and the chloro substituted derivatives thereof.

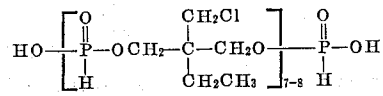
The following examples are illustrative.

EXAMPLE A

Condensation product of equimolar quantities of phosphorus trichloride and 1,1,1-trimethylolpropane

(A) Phosphorus trichloride (1.0 mole) is added portionwise to 1.0 mole of 1,1,1-trimethylolpropane at a temperature from about 100 to 135° C. with continuous nitrogen purge of the reaction mixture. The reaction mixture is then maintained under continuous nitrogen purge at a temperature from 100 to 125° C. until the evolution of hydrogen chloride had diminished. The pot residue was a colorless viscous liquid and was solid upon cooling to room temperature. The residue was subjected to infrared analysis. It was observed that the infrared spectrum of the solid showed an O—H band at 2.9 microns, a P=O band at 7 to 8 microns, a P—H band at 4.1 to 4.2 microns, a C—OH band at 9.3 microns and a C—Cl band at 13.5–13.7 microns.

(B) The pot residue obtained above was subjected to progressively increasing pot temperatures at progressively decreasing pressures in a distillation system equipped with an eleven inch Vigreux column equipped with a heating tape until a temperature of 175° C. at 0.5 to 1 mm. of mercury pressure was reached. Distillation was continued at this temperature and pressure until the residue reached a constant weight. The resulting still residue was a solid clear resinous polymer softening at about 80° C. and having a molecular weight (osmometry) of from about 1250 to 1750. The polymeric product decomposes in contact with air at about 245 to 255° C. and is ascribed the formula



Elemental analysis:

	C	H	P	Cl
Calculated	34.3	5.9	16.8	16.8
Found	33.93	6.24	16.25	15.8

Infrared analysis indicates P=O, P—H and O—H. There was poor resolution throughout the spectrum particularly in the 9.5 to 10.5 micron region. To check out the possibility of P—Cl bonding, an ethanolic solution of the polymer was treated with aqueous silver nitrate. No precipitate was formed. This made the existence of such a bond unlikely, since chlorine should be quite reactive under these conditions.

EXAMPLE B

A mixture of equal parts by weight of the polymeric product of the process of part (A) above and a mixture of equal parts by weight of propylene glycol and 2-methylpentane-1,3-diol is heated at 120 to 150° C. for 15 to 30 minutes and the reaction mixture allowed to cool to room temperature. The reaction product separates into two phases which are separated and the lower density phase discarded. The higher density phase containing the desired phosphorus-containing polymeric product can be employed as extreme pressure additive in the functional fluids of the present invention without further treatment. If desired, the polymeric product so treated can be subjected to vacuum stripping at progressively increasing pot temperatures and progressively decreasing pressures in a distillation system equipped with an efficient column until a temperature of 175° C. at 0.5 to 1.0 mm. of mercury pressure and a constant still residue weight is reached.

In the following examples the polyglycol derivatives have been designated by letters A through L. The formulations which correspond to these designations are as in Table I below.

TABLE 1

Polyglycol A	Butyl ether of polypropylene glycol having an average molecular weight of about 1025.
Polyglycol B	Butyl ether of mixed oxyethylene-oxypropylene glycol having an average molecular weight of about 1000.
Polyglycol C	Butyl ether of ethoxy-polypropylene glycol having an average molecular weight of about 700.
Polyglycol D	Butyl ether of polypropylene glycol having an average molecular weight of about 1,600.
Polyglycol E	Butyl ether of ethoxy-polypropylene glycol having an average molecular weight of about 800.
Polyglycol F	Butyl ether of mixed oxyethylene-oxypropylene glycol having an average molecular weight of about 400.
Polyglycol G	Butyl ether of polypropylene glycol having an average molecular weight of about 675.
Polyglycol H	Butyl ether of polypropylene glycol having an average molecular weight of about 2,100.
Polyglycol I	Butyl ether of mixed oxyethylene-oxypropylene glycol having an average molecular weight of about 525.
Polyglycol J	Butyl ether of mixed oxyethylene-oxypropylene glycol having an average molecular weight of about 1,700.
Polyglycol K	Butyl ether of mixed oxyethylene-oxypropylene glycol having an average molecular weight of about 2,900.
Polyglycol L	Butyl ether of polypropylene glycol having an average molecular weight of about 350.

In addition those fluids designated such as polypropylene glycol 425 will be understood to indicate polypropylene glycol having an average molecular weight of 425, and the like.

The effectiveness of the various complex phosphorous containing polymeric products as extreme pressure additives in various types of functional fluids was tested on a Falex machine with standard test pins and "V" blocks. The test procedure consists in automatically loading the machine to 500 pounds per square inch and observing the torque at the initial loading and at three and five minute intervals. After the five minute break-in period under a load of 500 pounds, the automatic jaw loader is again placed in position and loading increased until failure occurs. A rapidly increasing torque and/or audible squealing is employed as end point indicating incipient failure. Breaking of the brass shear pin and loss of torque represents complete failure. Results of a number of tests are reported in Tables 2 through 9. The results are reported as failure in pounds per square inch of jaw load at incipient (squeal) and complete failure. All tests were performed at room temperature.

The improvement in load-carrying capacity resulting from admixing the extreme pressure additives with polyalkylene glycol derivatives is shown by Examples 1 through 8 of Table 2. Blends 4(a), 4(b), 5(a) and 5(b) of Table 2 represent functional fluids having viscometric characteristics suitable as automotive hypoid gear and transaxle lubricants. However, only blends 4(b) and 5(b) containing the extreme pressure additives have adequate load-carrying characteristics for this application. Blends 6(a) and 6(b) have viscometric properties desirable in turbo-prop and helicopter aircraft engine and gear box lubricants, but only blend 6(b) containing the extreme pressure additive has adequate load carrying capacity for this application.

TABLE 2

[The Extreme Pressure Additives in Polyglycol Derivative Synthetic Lubricants and Lubricant Mixtures Containing Polyglycol Derivatives]

Example	Base Lubricant, Wt. Percent	Percent by Weight of Extreme Pressure	Other Additives Weight Percent	Falex Failure Load in Pounds	Remarks
1(a)	Polyglycol A	None	None	1,400	Squeal at 1,250.[1]
(b)	do	1% [2]	do	2,150	
2(a)	Polyglycol B	None	do	1,550	Squeal at 1,250.
(b)	do	1% [3]	do	>4,500	4,500 lbs. is machine limit.
3(a)	Polyglycol C	None	do	1,100	Squeal at 900.
(b)	do	1% [4]	do	3,050	
4(a)	Polyglycol D, 30% Polyglycol E, 70%	None	2% PANA [5]	1,250	Squeal at 110.
(b)	Polyglycol D, 30% Polyglycol E, 70%	0.5% [3]	2% PANA	3,000	
5(a)	Polyglycol D, 74% Di-isooctyl Adipate 26%	None	1% PANA	1,450	Squeal at 1,250.
(b)	Polyglycol D, 74% Di-isooctyl Adipate 26%	0.5% [6]	1% PANA	>4,500	4,500 lbs. is machine limit.
6(a)	Polyglycol D, 30% Di-2-ethylhexyl Adipate 70%	None	2% PANA	1,600	Squeal at 1,450.
(b)	Polyglycol D, 30% Di-2-ethylhexyl Adipate 70%	1.0% [3]	2% PANA	3,400	
7(a)	Polypropylene Glycol 425	None	None	1,100	
(b)	do	0.5% [3]	do	3,100	
8(a)	Azelate Diester of Polyglycol F	None	do	1,450	Squeal at 1,250 p.s.i.
(b)	do	0.5% [3]	do	2,850	

[1] Squeal indicates incipient failure.
[2] Reaction product of pentaerythritol monolaurate and PCl_3 reached in approximately equimolar quantities.
[3] Reaction product obtained by reacting approximately equimolar portions of trimethylolpropane and PCl_3.
[4] Reaction product obtained by reacting approximately equimolar portions of trimethylolethane and PCl_3.
[5] N-phenyl-alpha-naphthylamine.
[6] Reaction product obtained by reacting approximately equimolar quantities of 1,2,6-hexanetriol and PCl_3.

TABLE 3

[Extreme pressure Additives in Ester-Type Synthetic Lubricants]

Example	Base Lubricant, Wt. Percent	Percent by Weight Extreme Pressure Additive	Other Additive(s) Weight Percent	Falex Failure Load in Pounds	Remarks
9(a)	Di-2-ethylhexyl azelate	None	None	1,500	Squeal at 1,250.[1]
(b)	do	2.0% [2]	do	2,800	
10(a)	Di-2-ethylhexyl sebacate	None	do	1,660	Squeal at 1,400.
(b)	do	0.1% [3]	do	2,900	
(c)	do	0.5% [3]	do	2,400	
(d)	do	5% [3]	do	3,000	
11(a)	Di-2-ethylhexyl phthalate	None	do	1,550	
(b)	do	1.0% [3]	do	1,850	
12(a)	Mixed Adipate Fluid, A[4]	None	do	1,400	Squeal at 1,300.
(b)	Mixed Adipate Fluid A	0.25% [3]	do	2,850	
(c)	do	1.0% [3]	do	3,550	
(d)	do	0.5% [5]	0.5% PHTZ [6] 0.5% Q [7]	2,800	
(e)	do	0.25% [8]	1.0% PANA [9] 0.01% Q [7]	3,100	
13(a)	Dipropylene Glycol Dipelargonate	None	None	1,500	Squeal at 1,450 p.s.i.
(b)	do	0.5% [4]	do	4,100	

[1] A squealing noise indicates incipient failure.
[2] Reaction product of approximately equimolar quantities of trimethylolethane and PCl_3.
[3] Reaction product of approximately equimolar quantities of trimethylolpropane and PCl_3.
[4] 30 weight per cent Di-isodecyl Adipate, 69 weight percent Di-isooctyl Adipate, and 1 weight per cent Polyoxypropylene Glycol monobutyl ether.
[5] Reaction product of approximately equimolor quantities of 2-ethyl-2-methyl-1,3-propanediol and PCl_3.
[6] Purified phenothiazine.
[7] Quinizarin.
[8] Reaction product of approximately equimolar quantities of 1,2,6-hexametriol and PCl_3.
[9] N-phenyl-alpha-naphthylamine.

TABLE 4

[Extreme pressure additives in petroleum base lubricants]

Example	Base Lubricant	Percent by Weight [1] Extreme Pressure Additive	Falex Failure Load in Pounds
14(a)	SAE 10 Mineral Oil [2]	None	400
(b)	SAE 10 Mineral Oil	1.0	1,900
15(a)	SAE 90 Mineral Oil	None	500
(b)	do	0.05	1,750
(c)	do	10.0	3,750
(d)	do	1.0	2,000

[1] Reaction product of equimolar quantities of monolauryl-timethylol propane and PCl_3.

[2] Mid-continent base solvent extracted oil having viscosities of 46.3 and 148 SUS at 210° F., and 100° F. respectively.

TABLE 4a

[Extreme pressure additives in petroleum oil-synthetic lubricant blends]

Example	Base Lubricant (Volume Percent)	Percent Extreme Pressure Additive	Falex Test: Load in Pounds/Square Inch at Failure
16(a)	70% (60% 200 SUS at 100° F. Paraffinic Neutral; 40% 71 SUS at 100° F. Naphthenic Neutral); 30% Polyglycol E (containing 0.5% V.I. Improver [1] and 2% N-phenyl-a-naphthylamine)	None	950
(b)	Same as in Example 16(a)	0.25% [2]	1,500
(c)	Same as in Example 16(a)	0.25% [3]	1,750
17(a)	65% 146 SUS at 100° F. Paraffinic Neutral; 30% Polyglycol E [4]; 4.5% Di-(isodecyl) adipate; 0.5% V. I. Improver, Pour Point Depressant	None	1,000
(b)	Same as in Example 17(a)	0.5% [3]	2,150

[1] Polymethacrylate, type sold commercially under the Trademark "Acryloid 710."

[2] Reaction product of approximately equimolar quantities of trimethylolethane and PCl_3.

[3] Reaction product of approximately equimolar quantities of trimethylolpropane and PCl_3.

[4] Contains as an antioxidant 2 percent N-phenyl-a-naphthylamine.

TABLE 5

[Mixtures of the Complex Phosphorus-Containing Compounds (EPA) in Various Hydroxy-Containing Compounds (OH) as Extreme Pressure Additives in Polyglycol Derivative Synthetic Lubricants and in Lubricant Mixtures Containing Polyglycol Derivatives]

Example	Composition of "OH-EPA" Compound Weight Percent	Weight Percent "OH-EPA" Compound Admixed with Base Fluid	Base Lubricant Weight Percent	Other Additives (Weight Percent)	Falex Test: Load in Pounds/Square Inch at Failure [1]
18 (a)		None	Polyglycol G	None	1,750
(b)	50% EPA [2] in 2-methylpentane-1,3-diol.	1	do	do	4,200
19 (a)		None	Polyglycol B	do	1,550
(b)	50% EPA [2] in 50-50 weight percent Mixture of Propylene Glycol and 2-methylpentane-1,3-diol.	1	do	do	4,300
20 (a)	Same as Example 19	None	Polyglycol D, 26%; Di-isodecyl Adipate 74%	do	1,550 (1,400)
(b)		1	Polyglycol D 26%; Di-isodecyl Adipate 74%	do	3,200
21 (a)	Same as Example 19	None	Polyglycol H, 30%; Di-2-ethylhexyl sebacate 70%	2% PANA [3]	1,600
(b)		1	Polyglycol H, 30%; Di-2-ethylhexyl sebacate 70%	2% PANA	3,300
22 (a)		None	Polyglycol D, 30%; Polyglycol E, 70%	2% PANA	1,250 (1,100)
(b)	Same as Example 19	1	Polyglycol D, 30%; Polyglycol E, 70%	2% PANA	3,250
23 (a)		None	Mineral Oil-Synthetic Lube Blend #10-144.	See note (4)	950
(b)	50% EPA [2] in 2-ethylhexane-1,3-diol	1	Same as in Example 23(a)	See note (4)	1,600
24 (a)	Same as Example 19	50	Water	See note (5)	3,900

[1] Number in parenthesis refers to load in pounds/square inch at incipient failure (squealing audible).

[2] Reaction product of approximately equimolar quantities of trimethylolpropane and PCl_3.

[3] N-phenyl-alpha-naphthylamine.

[4] A blend of 70 weight percent of a solvent-refined naphthenic base petroleum oil having viscosities of 4.35 cs. and 26.4 cs. at 210° F. and 100° F. respectively, 27.5 weight percent Polyglycol E, 2.0 weight percent n-phenyl-alpha-naphthylamine and 0.5 weight percent polymethacrylate pour point depressant.

[5] Corrosion inhibitors normally employed in aqueous-base functional fluids such as sodium or potassium nitrate, borax, or the various alkali metal phosphates, may be used.

TABLE 6

[Mixtures of Complex Phosphorus Containing Extreme Pressure Additive (EPA)[1] From PCl_3 and Trimethylolpropane in Hydroxy-Containing Compounds (OH)/Admixed in an Adipate Base Fluid[2]]

Example	Composition of "OH-EPA" Compound Weight Percent	Weight Percent "OH-EPA" Compound Admixed with Base Fluid	Other Additives (Weight Percent)	Falex Test: Load in Pounds/Square Inch at Failure[3]
25(a)	10% EPA in Propylene Glycol	None	0.5 Phenothiazine 0.05	1,400 (1,300)
(b)	Same as in Example 24(a)	3	Same as in Example 24(a)	2,350
(c)	Same as in Example 24(a)	3	1.0 N-phenyl-2-naphthylamine 0.05 Quinizarin	2,550
26	Same as in Example 24(a)	3	0.5 Phenothiazine	2,650
27	50% EPA in Propylene Glycol	1.0	0.5 Phenothiazine 0.05 Quinizarin	2,450
28	20% EPA in Dipropylene Glycol	3.0	0.5 Phenothiazine 0.05 Quinizarin 0.1 Dicyclopentadienedioxide	2,050
29	50% EPA in Butylene-1,3-glycol	1.0	0.5 Phenothiazine 0.05 Quinizarin	2,350
30	50% EPA in 2-methylpentane-1,3-diol	1.0	1.0 N-phenyl-2-naphthylamine 0.05 Quinizarin	2,250
31(a)	10% EPA in 50/50 mixture of propylene glycol and 2-methylpentane-1,3-diol.	3.0	0.5 Phenothiazine 0.05 Quinizarin	2,750
(b)	Same as in 31(a)	None	0.5 Phenothiazine 0.01 Quinizarin	1,350 (1,300)
32(a)	50% EPA in 50/50 mixture of propylene glycol and 2-methylpentane-1,3-diol.	0.05	0.5 Phenothiazine 0.01 Quinizarin	----------
(b)	do	0.1	1.0 N-phenyl-a-naphthylamine 0.05 Quinizarin	2,000
33	Same as in Example 32	0.25	1.0 N-phenyl-a-naphthylamine 0.01 Quinizarin	2,400
34	do	0.50	0.5 N-phenyl-a-naphthylamine 0.01 Quinizarin	2,500
35	do	1.0	0.5 N-phenyl-a-naphthylamine 0.01 Quinizarin	2,600
36	do	4.0	None	2,200
37		None	0.5 N-phenyl-a-naphthylamine 0.01 Quinizarin	1,350
38		None	0.5 N-phenyl-a-naphthylamine 0.01 Quinizarin	1,350 (1,300)
39		None	None	1,400 (1,300)
40	Same as in Example 32	1.0	do	2,400
41	do	0.1	0.5 N-phenyl-a-naphthylamine 0.01 Quinizarin	2,000
42	do	5.0	0.5 N-phenyl-a-naphthylamine 0.01 Quinizarin	1,850
43	2% EPA in Polyglycol D	26	None	2,100
44	10% EPA in Polypropylene Glycol 425	3.0	0.5 Phenothiazine 0.05 Quinizarin 0.1 Dicyclopentadiene dioxide	2,000
45(a)	10% EPA in Polyglycol L	3.0	0.5 Phenothiazine 0.05 Quinizarin 0.1 Dicyclopentadiene dioxide	2,250
(b)	Same as in Example 45(a)	None	0.5 Phenothiazine 0.05 Quinizarin 0.1 Dicyclopentadiene dioxide	1,350 (1,250)
46	10% EPA in Polyglycol I	3.0	0.5 Phenothiazine 0.05 Quinizarin	2,850
47	50% EPA in Polyglycol I	1.0	0.5 Phenothiazine 0.05 Quinizarin	2,700
48	10% EPA in Polyglycol J	3.0	0.5 Phenothiazine 0.05 Quinizarin	>4,500
49	10% EPA in Polyglycol K	2.0	0.5 Phenothiazine 0.05 Quinizarin	1,900
50	10% EPA in Tripropylene Glycol monomethyl ether.	3.0	0.5 Phenothiazine 0.05 Quinizarin	2,600

[1] Extreme pressure additive was obtained by contacting trimethylolpropane and PCl_3 as hereinbefore described. The reaction mixture was then stripped in a Vigreux column to obtain the concentrated polymer product.

[2] Base fluid comprising 30 weight percent di(isodecyl) adipate, 69 weight percent di(isooctyl) adipate and 1 weight percent UCON LB-1715; a monoalkyl ether of a polyalkylene glycol having an SUS viscosity of 17.5 at 100° F.

[3] Number in parentheses refers to load in pounds/square inch at incipient failure (squealing sound).

TABLE 7

[Mixtures Of Extreme Pressure Additives In (OH)-Containing Compounds/Admixed in An Adipate Base Fluid[1]]

Example	Composition of OH-EPA Compound (Weight Percent)	Weight Percent "OH-EPA" Compound Admixed with Base Fluid	Other Additives (Weight Percent)	Falex Test: Load in pounds/Square Inch at Failure
51	50% Reaction product of approx. equimolar quantities of trimethylolethane and PCl_3 in Butylene-1,3-glycol.	0.5	1.0 N-phenyl-a-naphthylamine 0.01 Quinizarin	1,800
52	50% Reaction product of approx. equimolar quantities of 1,2,6-hexanetriol and PCl_3 in Butylene-1,3-glycol.	0.5	1.0 N-phenyl-a-naphthylamine 0.01 Quinizarin	2,500
53	50% Reaction product of approx. equimolar quantities of trimethylolethane and PCl_3 in Oleyl Alcohol.	0.5	1.0 N-phenyl-a-naphthylamine	2,000
54	50% Reaction product of approx. equimolar quantities of trimethylolethane and PCl_3 in Glycolic Acid.	0.5	1.0 N-phenyl-a-naphthylamine 0.01 Quinizarin	2,700

[1] Base fluid comprising 30 weight percent di(isodecyl) adipate and 1 weight percent polyglycol L, a polyoxyalkylene monoalkyl ether having an SUS viscosity of 1,715 at 100° F.

TABLE 8

[Mixtures Of Extreme Pressure Additives (EPA) In (OH)-Containing Compounds/Admixed In Ester-Type Base Fluids]

Example	Base Fluid	Composition of "OH-EPA" Compound (Weight Percent)	"OH-EPA" Compound Admixed in Base Fluid (Weight Percent)	Other Additives (Weight Percent)	Falex Test: Load in Pounds/Square Inch at Failure [1]
55(a)	Di(2-ethylhexyl)Sebacate	50% EPA [2] in 50/50 mixture of propylene glycol and 2-methyl-pentane-1, 3-diol.	None	None	1,600 (1,400)
(b)	do		None	1.0 N-phenyl-a-naphthylamine, 0.05 Quinizarin	1,600 (1,400)
(c)	do		1.0	1.0 N-phenyl-a-naphthylamine, 0.05 Quinizarin	3,400
56(a)	Di(isodecyl)Adipate (isodecanol from Oxo Process).	50% EPA [3] in ricinoleic acid	None	1.0 N-phenyl-2-naphthylamine	1,400
(b)	do		0.5	1.0 N-phenyl-a-naphthylamine	2,750
57(a)	Di(2-ethylhexyl)Azelate	Same as in Example 55	None	1.0 N-phenyl-a-naphthylamine, 0.5 Quinizarin	1,500 (1,100)
(b)	do		1.0	1.0 N-phenyl-a-naphthylamine, 0.05 Quinizarin	3,500
58(a)	Azelate Diester of Polyglycol F	10% EPA [2] in polypropylene Glycol 425.	None	None	1,100
(b)	do		1.0	do	3,000

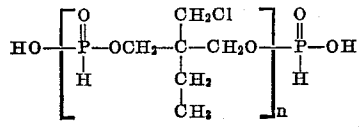
[1] Number in parenthesis load in pounds/square inch at incipient failure (squealing sound).

[2] Reaction product of approximately equimolar quantities of trimethylolpropane and PCl_3.

[3] Reaction product of approximately equimolar quantities of trimethyl olethane and PCl_3.

What is claimed is:

1. A functional fluid composition which comprises a major proportion of an organic functional base fluid of lubricating viscosity and a minor amount, sufficient to improve the load carrying properties of said composition, of a polymer of the formula:



wherein *n* represents a number having a value such that said polymer has a molecular weight of from about 400 to about 12,000.

2. The functional fluid composition of claim **1** wherein said composition contains a minor amount, sufficient to improve the solubility characteristics of said polymer in said base fluid, of a member selected from the group consisting of alkanols, polyhydroxyalkanes, polyalkylene glycols, monoalkyl ethers of alkylene glycols and polyalkylene glycols, monoalkanoic acid esters of alkylene glycols and polyalkylene glycols, and aliphatic hydroxy acids.

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