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HYDRAULIC FLUIDS AND LUBRICATING COMPOSITIONS

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6 Claims. (Cl. 252—75)

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This invention is directed to lubricating compositions and hydraulic fluids having improved technical properties. More particularly, the invention pertains to such compositions containing components imparting improved low temperature properties, corrosion resistance and low flammability.

Current developments in aviation and industrial fields require the use of lubricants and hydraulic fluids having high resistance to corrosion, low flammability, and especially improved properties at the low operating temperatures which are encountered, for example, during the operation of aircraft, and the like. Numerous proposals have been made for correcting one or another of these properties, but such correction is usually effected at the expense of another property of the fluids. For example, the use of aryl phosphates, such as tricresyl phosphate, as a hydraulic fluid is satisfactory only at moderate temperatures due to the high sensitivity of said phosphates to thermal influences. The aryl phosphates, however, are beneficial in having great resistance to flammability. Heavy mineral oils may be used in similar situations, but are of limited use under cold conditions due to their high pour points. Alkyl phosphates may be used under certain limited conditions in an unmodified state, but are usually unsuitable for lubricating purposes and the like due to their mediocre resistance to flammability and their inherent low viscosity. Mixtures of lubricants have been suggested, but heretofore such combinations have been limited due, for example, to the relatively low miscibility of aryl phosphates with mineral lubricating oils.

It is an object of the present invention to provide improved lubricants for use at both low and high temperatures. It is another object of this invention to provide improved hydraulic fluids and lubricating compositions combining in an optimum degree the properties of high non-flammability and low response to thermal changes. Other objects will become apparent during the following discussion.

Now in accordance with the present invention, it has been found that the above and other objects may be accomplished by combining high viscosity index "bright stock" with normally liquid aliphatic phosphorus esters. More specifically, the compositions of the present invention comprise from about 7.5% to about 60% by weight of a high viscosity index bright stock and from about 40% to about 92.5% of an aliphatic ester of a phosphorus acid.

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THE COMPOSITIONS

The compositions of this invention comprise two main ingredients as generally referred to above. In their preferred embodiments, the hydraulic fluids of this invention comprise from about 30 to about 50% by weight of a bright stock and from about 50% to about 70% by weight of an aliphatic ester of a phosphorous acid. While these compositions are preferred for use as hydraulic fluids, somewhat different mixtures are more suitable for use as aircraft turbo-prop or turbo-jet lubricants. The latter preferably contain from about 9 to about 20% of bright stock and from about 80 to about 91% of an aliphatic ester of a phosphorus acid. In both types of compositions the preferred ester is a tri-alkyl phosphate, which will be defined more fully hereinafter. Optimum properties are obtained, however, if the tri-alkyl ester contains alkyl groups having at least 6 carbon atoms and usually between about 6 and about 12 carbon atoms each, the total carbon atom content of each molecule thus being at least about 18 carbon atoms.

In addition to the two principal components which are the essential features of this invention, other ingredients may be added in order to provide desirable properties. An especially effective type of additive for the prevention of corrosion under oxidizing conditions in this particular mixture of liquids comprises the metallic salts of condensation products of formaldehyde with alkyl phenols; preferably the calcium salt is employed. A synergistic effect has been found to occur in this composition when the latter additive is combined with an aromatic amine such as phenyl alpha naphthylamine. In addition, other important additives finding use with certain of the subject compositions comprise especially pour point depressants such as the polymerized esters of the acrylic acid series and the like, especially aliphatic esters of polymerized methacrylic acid.

BRIGHT STOCK

While the present invention is not to be confined to the use of a mineral oil derived from any particular source or by any particular refining process, the usual source of suitable mineral oils comprises the fraction thereof generally termed "bright stocks," and particularly bright stocks having a viscosity index of at least 60. The term "bright stock" is one which is well recognized in the art of refining mineral oils. To obtain the desired fraction, crude oils are usually subjected to distillation under ordinary pressures in order to obtain a "long residue" comprising the frac-

tion which does not distill under these conditions without substantial decomposition. The long residue is then subjected to steam distillation, usually under a vacuum. Under these conditions, gas oil and waxy lubricant fractions distill over, leaving what is normally termed a "short residue" or a "steam refined stock," also known as "cylinder stock." The steam refined stock is then deasphalted (if an asphaltic crude is employed) and subjected to dewaxing operations to remove microcrystalline or macrocrystalline waxes. Following this, the raffinate is treated with a solvent for the purpose of reducing or removing the aromatic fractions. Clay contact treatment or percolation may be employed to clean up the oil following any one or all of these separate operations. The raffinate which remains after deasphalting, dewaxing, extraction, and clay treatment is generally called "bright stock."

The bright stocks suitable for use in the present compositions should have the following ranges of properties:

Table I

PROPERTIES OF BRIGHT STOCKS

Viscosity, S. U. S., 100° F. >1250, usually 1250–11,000, preferably 1500–3500
Viscosity, S. U. S., 210° F. >75, usually 125–325, preferably 150–250
Viscosity index > +60, preferably +85–110
Aniline point, °C. >100, preferably >115
Flash, °F. >475, preferably >500
Fire, °F. >550, preferably >600
Pour point, °F.—maximum 25, preferably lower than 15
Percent aromatics <15, preferably <10 opt. <5
Percent naphthenes <35
Percent paraffines, at least 60

The tables which follow give the properties of typical bright stocks which are useful in the compositions of this invention.

vention is predicated upon the use of a mineral oil fraction having the above defined ranges of properties and not upon the source or treatment of such oil.

The two most important inherent properties of a mineral oil suitable for the present use comprise the aromatic content and the viscosity characteristics. The aromatic content has a large influence upon the sensitivity of the oil to thermal changes and the viscosity of the oils defines their suitability for their present purpose. Hence, the best definition with respect to essential characteristics of mineral oil suitable for the present compositions comprises those having an aromatic hydrocarbon content less than about 15% by weight and having a viscosity of between about 1250 and about 11,000 SUS at 100° F. Having defined these particular properties, the other properties such as flash, fire, aniline point, and viscosity index usually are largely dependent upon them.

THE PHOSPHORUS ESTERS

The phosphorus esters useful for inclusion in the present compositions comprise the normally liquid aliphatic esters of acids of phosphorus. While the trialkyl phosphates are particularly preferred, other classes are suitable in addition to or in place of said phosphates. These include dialkyl hydrocarbon phosphonates, especially dialkyl alkanephosphonates, alkyl dialkanephosphinates, diphosphorus compounds such as bis (dialkyl phosphono) alkanes, bis(alkyl alkane phosphino) alkanes, alkane diol bis(dialkane phosphinate), alkane diol bis(dialkyl phosphates), alkane diol bis(alkyl alkane phosphonates) and the corresponding ethers of the above diphosphorus compounds. Classes of the latter which are included are bis(dialkyl phosphono alkyl) ethers, bis(alkyl alkanephosphinico alkyl) ethers and bis(dialkyl phosphato alkyl) ether.

The phosphorus esters which are particularly useful in these compositions ordinarily have a total of at least 18 carbon atoms per molecule; preferably this total is between about 20 and about 32 carbon atoms per molecule. Typical trialkyl phosphates which are especially suitable contain alkyl radicals having from about 6 to about 12 carbon atoms each and include the following:

Trihexyl phosphates
Triheptyl phosphates
Tricotyl phosphates, e. g.,
Tri(2-ethylhexyl) phosphate OR
Tri(isooctyl) phosphate
Trinonyl phosphates, e. g.,
Tri(3,5,5-trimethylhexyl) phosphate
Tridecyl phosphates
Tridodecyl phosphates
Dihexyl octyl phosphate

Table II

EXAMPLES OF TYPICAL BRIGHT STOCKS

	SUS		Viscosity Index	Ring Analysis			Ratio of Paraffines to Naphthenes	Average Mol Weight	Average Rings per Mol
	100	210		Aromatic	Naphthenes	Paraffines			
Mid-Continent Bright Stock—Conventional Extraction	3,650	164	77	13	17	70	4.1	685	3.7
Mid-Continent Bright Stock—Mild Extraction	2,569	141	85	9	19	72	3.8	685	3.4
Mid-Continent Bright Stock—Heavy Extraction	2,049	131	93	3	21	76	3.62	675	2.9
Pennsylvania Bright Stock	2,109	144	102	5	16	79	4.95	730	3.0
Coastal Bright Stock	1,251	85	63	4	35	61	1.74	515	3.4

Table III

SPECIFICATIONS FOR TYPICAL MID-CONTINENT BRIGHT STOCKS

	Unfiltered		Filtered
Gravity, °API, minimum	25.5	24.5	25.5
Color, NPA	8+	Dark Green	6.7
Pour Point, ° F., maximum	10	10	10
Flash ° F., minimum	540	580	545
Fire ° F., minimum	615	655	610
SUS 210° F	150–170	200–215	150–160
Viscosity Index, minimum	90	90	90

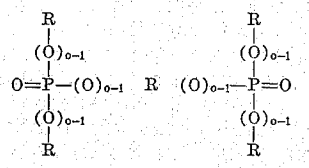
It will be understood from the above analyses that the source or treatment of a particular mineral oil is not as important for the present purpose as the final properties of the mineral oil constituent to be used in these compositions. For example, it is possible to vary the extent of solvent extraction dependent upon the original aromatic content and the requirements of the specific use of the final product, as well as upon the necessity or desirability of deasphalting, clay treating, acid treating, and the like. Hence, it will be recognized that the present in-

Typical species of phosphonates and phosphinates are given below:

Dialkyl hydrocarbon phosphonates:
- Di(2-ethylhexyl) hexanephosphonate
- Dihexyl hexanephosphonate
- Dioctyl(3,5,5 - trimethylhexane) phosphonate
- Dihexyl benzenephosphonate

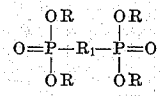
Alkyl dialkane phosphinates:
- Butyl di(2-ethylhexane) phosphinate
- Hexyl diheptane phosphinates

Referring now to the diphosphorus compounds, these may be represented with the following general formula:



wherein each R is an aliphatic hydrocarbon radical.

The above classification of diphosphorus compounds includes especially substituted aliphatic hydrocarbons bearing 2 phosphorus radicals in the form of phosphate, phosphonate, phosphinate, or phosphine oxide groups. One of the more preferred classes of liquids suitable for use, according to the present invention, includes the bis(dialkyl phosphono) alkanes. These have the general configuration of



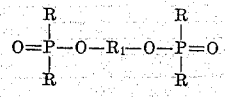
Preferably R_1 in the above formula is an alpha, omega-alkylene hydrocarbon radical of at least 3 carbon atoms. Each of the other R substituents may be a hydrocarbon radical of such nature that the entire compound is substantially fluid at operating temperatures. Preferably each of these groups contains from 3 to 9 carbon atoms each, and still more preferably at least two of them are of branched configuration. The following suitable species are typical of this presented configuration:

Bis-1,3-(diisobutyl phosphono) propane
Bis-1,4-(diisopropyl phosphono) butane
Bis-1,5-[di(3-methylbutyl) phosphono] pentane
Bis-1,6-[di(2-ethylhexyl) phosphono] hexane
Bis-1,3-[di(3,5,5-trimethylhexyl) phosphono) propane

The alkylene group separating the two phosphorus radicals may be shorter than about 12 carbon atoms or may be of branched configuration as typified by the following species:

Bis-1,2-(di-tert-butyl phosphono) ethane
Bis-1,2-(di-tert-butyl phosphono) -3,4-dimethylpentane
Bis-2,4-(di-sec.-butyl phosphono) -3,5-dimethylhexane
Bis-1,6-(di-n-pentyl phosphono) -3,4,5-trimethylhexane

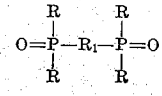
Another suitable subgeneric group of phosphorus compounds useful in the practice of this invention comprises the alkanediol bis(dialkane phosphinates). These materials have the general configuration:



The preferred configurations and carbon contents of the individual portions of this and the following classes are in general those given in the foregoing description of the bis(dialkyl phosphono) alkanes except where especially noted. Preferably the substituent R_1 contains from 3 to 9 carbon atoms while the remaining R's have from 4 to 9 carbon atoms each. The following species are typical of this class:

1,5-pentanediol bis-[di(2-ethylhexane) phosphinate]
1,6-hexanediol bis-[di(2-isobutane) phosphinate]
1,7-heptanediol bis-(di-n-butanephosphinate)
3,4-heptanediol bis-[di(3,5,5 - trimethylhexane) phosphinate]
2,5-hexanediol bis-(dipentanephosphinate)

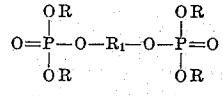
Another class of compounds coming within the general scope of this invention are the tetraalkylalkylenediphosphine oxides. These materials have the following general formula:



The following species are typical of this class of compounds:

Tetra-n-butylhexamethylenediphosphine oxide
Tetra-tert-butylpentamethylenediphosphine oxide
Tetra-sec-butyl(3,5,5- trimethylhexylene) diphosphine oxide
Tetra-tert - amylheptamethylenediphosphine oxide
Tetra-isopropylpentamethylenediphosphine oxide

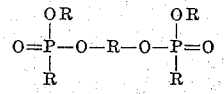
Another class of useful diphosphorus derivatives includes the alkanediol bis-(dialkyl phosphates) having the following general configuration:



The following list of suitable species illustrates this group:

1,6-hexanediol bis(dibutyl phosphate)
3-methyl-1,6-hexanediol bis(di-tert-butyl phosphate)
2,3-diethyl-1,6-hexanediol bis(di-sec-amyl phosphate)
2,4,4-trimethyl - 1,5-pentanediol bis(di-3,5,5 - trimethylhexyl phosphate)
1,4-butanediol bis(diisopropyl phosphate)

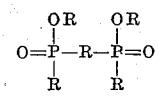
Another sub-generic class constitutes alkanediol bis(alkyl alkanephosphonates) which have the general configuration:



The suitable species which follow illustrate the nature of this class:

1,5-pentanediol bis-(butyl butanephosphonate)
1,4-butanediol bis-(tert-butyl 2-methyl-1-propanephosphonate)
1,6-hexanediol bis-(3,5,5-trimethylhexyl butanephosphonate)
3,4-dimethyl-1,6-hexanediol bis-(tert-amyl pentanephosphonate)
1,2-ethanediol bis-(3,5,5-trimethylhexyl butanephosphonate)

Another class of compounds to be considered includes bis-(alkyl alkanephosphinico) alkanes which have the general configuration:



This class is exemplified by the following species:

Bis-1,2-(n-butyl butanephosphinico) ethane
Bis-1,3-(tert-butyl butanephosphinico) propane
Bis-1,4-(sec-amyl pentanephosphinico) butane
Bis-1,5-(3,5,5-trimethylhexyl 2,4,4-trimethylpentenephosphinico) butane
Bis-1,6-(n-hexyl 1-methyl - 1-propanephosphinico) hexane

It will be understood that symmetrical compounds are not necessary for the operation of the present invention. For example, the various substituents denoted as R in the above general formulae may vary within a given compound, both with respect to carbon atom content and to spatial configuration. The branched configurations are favored due to their generally superior effect upon the lubricating characteristics, especially at low temperatures. Unsaturated hydrocarbon radicals are especially to be desired when they are directly attached to a phosphorus atom since their presence has been found to improve the corrosion characteristics of lubricants prepared therefrom. Additionally, while the two end groups may be identical in a single compound for specific purposes, it is sometimes desirable to include two different types of phosphorus end groups in order to obtain the beneficial properties attributable to each type. Suitable illustrating compounds having mixed end groups are as follows:

1 - (butyl butanephosphinico) - 2 - (di - sec-butyl phosphono) ethane
1 - (di - 2 - ethylhexanephosphinate) - 5 - (dibutyl phosphate) pentanediol

Typical species of the corresponding ethers of di-phosphorus compounds are the following:

Bis-[(di-amylphosphono) methyl] ether
Bis-[(di-laurylphosphono) ethyl] ether
Bis-[(butyl hexanephosphinico) ethyl] ether
Bis-[(di-isopropyl phosphono) amyl] ether

Details of the preparation and properties of these and other ethers will be found in copending application Serial No. 214,432 filed March 7, 1951, by Denham Harman et al.

The above classes of compounds may be prepared by the following typical methods:

The preparation of bis-(dialkyl phosphono)-alkanes illustrates the conditions necessary for the preparation of typical compounds. In this particular instance sodium is suspended in a suitable solvent (such as refluxing heptane) after which a dialkyl phosphite is added and refluxed for a period of 1 to 4 hours to form a sodium dialkyl phosphite. Subsequently a dibromoalkane is gradually added to the refluxing solution. After heating for 1 to 8 hours at reflux, the corresponding bis-(dialkyl phosphono) alkane has been formed. Sodium bromide is filtered off and the remaining solution is water washed, neutralized with dilute alkali, water-washed again and the volatile diluent is removed by topping to a temperature of about 150° C. at 150 mm. pressure. If a highly purified product is desired the bottoms from this topping operation may then be distilled in a molecular still to obtain a purified product as distillate.

The preparation of alkanediol bis-(dialkyl phosphate) is preferably effected by reaction of an alkylene glycol with a dialkyl chlorophosphate in the presence of a hydrogen chloride acceptor. Preferably the components are added to one another at a temperature between about −10° C. and +20° C. and then warmed on a steam bath for a period of time between about 1 hour and 16 hours, preferably between 2 and 4 hours. Typical hydrogen chloride acceptors are amines, such as trimethylamine, pyridine, or dimethylaniline. Alternatively, the hydrogen chloride evolved during the reaction may be removed as it is formed by a current of air. Following the reaction, the mixture is water-washed to remove hydrochloride salts or the salts (such as pyridine hydrochloride) may be removed by filtration. The mixture is then washed with dilute hydrochloric acid to remove any excess base which may be present. Purification may be completed by distillation of the volatile constituents leaving the desired phosphate compounds.

In the preparation of the tetra-alkylalkylenediphosphine oxides, the following conditions have been found to be suitable: A tetra-alkyl diphosphonoalkane is treated with phosphorus pentachloride at a temperature between 75° and 100° C. for a period of time, preferably between 2 and 4 hours. The product of this reaction is a tetrachlorodiphosphonoalkane. This product is then treated with a Grignard reagent (an organo magnesium halide) at a temperature between 0° and 25° C. for a period of 2 to 4 hours. The resulting product is the desired bis-phosphine oxide.

A suitable preparation for bis-(alkyl alkanephosphinico) alkanes comprises treatment of a dialkyl alkanephosphonite with a dibromoalkane under the conditions of the well-known Arbuzov reaction.

One property of this general class of diphosphorus derivatives distinguishing them from the more commonly employed monophosphates, such as trioctyl phosphate, is their exceptional behavior with respect to corrosion. These materials have been found to be substantially noncorrosive with respect to copper, magnesium, iron, cadimium, or aluminum. As a class, the diphosphorus compounds described hereinbefore have suitable properties for use as hydraulic fluids. In general, their viscosities are between 10 and 25 centistokes at about room temerature. The derivatives bearing 4 alkane to 2 phosphorus linkages or 2 alkane to 1 phosphorus linkages have substantially higher viscosities making them especially suitable as synthetic lubricating oils. The latter compounds include especially alkanediol bis-(dialkanephosphinate).

The following table illustrates the unexpected properties of a typical composition coming within the definition of the present invention:

Table IV

PROPERTIES

	1	2	3
Trioctyl Phosphate, Percent	100		64
Bright Stock, Percent		100	36
Viscosity Index	90	98	130
Pour Point, ° F	−80	+27	−50
Flammability	14		17

This table shows that an unexpected result was obtained in the changes in three properties resulting from the combination of trioctyl phosphate with a typical bright stock. In the first place, the viscosity index of the blend is about 50% higher than the viscosity index of either of the components. The reason for this is obscure, but constitutes an unexpected and beneficial result adding substantially to the value of this combination of fluids. Secondly, it will be found from the above data that the pour point of the combined fluid is minus 50° F., while the pour point of bright stock itself was plus 27° F. As is well-known, when two fluids having different pour points are combined, it is usual to find that the pour point of the blend is only slightly below that of the higher pour point of one of the components. Hence, it was unexpected to discover that in this particular combination the resulting pour point of the blend was in fact 77° F. lower than that of the component having the higher pour point. Finally, this table shows an unexpected feature with respect to flammability. While this term is dependent upon the exact physical conditions under which the fluid is to be used, a test called the "Pipe Cleaner Flammability Test" has been devised for differentiating between fluids under standard conditions for this property. Under the conditions which will be described hereinafter, the addition of bright stock to tri-octyl phosphate actually reduced flammability instead of increasing it as would normally be expected. In other words, the addition of a mineral oil (which is normally regarded as relatively flammable) reduced the flammability of a phosphate ester, which is normally regarded as relatively non-flammable. Hence, the present invention is particularly predicated upon the unexpected findings in these three properties, namely, with respect to viscosity index improvement, blended pour point advantage and reduction in flammability.

METALLIC SALTS

In some applications the compositions as defined hereinbefore cause corrosion of certain metals, and under oxidizing influences exhibit an increase in viscosity under operating conditions. It was found that only certain specific classes of additives could be effectively used in correcting these phenomena. The most effective additive for the purpose comprises the metallic salts of condensation products of formaldehyde with alkyl phenols. While the preferred metal in this respect is calcium, other effective metals are alkaline earth metals such as barium and magnesium. These may be supplemented by heavy metal salts and alkali metal salts of the subject condensation products such as zinc, aluminum, copper, lead, iron, nickel, cobalt, manganese, chromium, tin, sodium, potassium and lithium.

The alkyl phenols are preferably those having at least one alkyl group with from 4 to 12 carbon atoms. The most effective members for the present purpose are tertiary alkyl phenols having from about 5 to about 9 carbon atoms per alkyl radical. The condensation product formed between these alkyl phenols and formaldehyde are generally prepared by heating one mol of the phenol with between about ⅔ and one mol of formaldehyde with a catalytic amount of an acid or base. Normally these metals are heated for periods between about one and three hours at a temperature between about 175 and 225° F. Subsequently a base such as lime may be added and heating continued for a similar length of time in order to form the metallic salt. Alternatively the salt may be formed simultaneously with condensation by utilizing the metallic base as the condensation catalyst. Preferably mineral oil is also present so that the resulting product is obtained in the form of an oil concentrate ready for addition to liquid compositions. Further details of this type of product are to be found in U. S. Patent 2,250,188 issued July 22, 1941, to Chester E. Wilson.

In improving the compositions of this invention by the use of such salts, amounts between about 0.25% and about 5% by weight may be used. Under these conditions an effective reduction in metallic corrosion may be obtained. The following table illustrates the properties of a typical composition containing about 1.0% of a calcium salt of the condensation product formed between formaldehyde and amyl phenol.

Table V

Trioctyl phosphate, wt. per cent	60
Bright stock, wt. per cent	39.0
Calcium salt, wt. per cent	1.0
Viscosity Cs. 100° F.	33.09
Viscosity Cs. 210° F.	5.77
Viscosity index	126
Pour point, °F.	−25
Acid Neut. No.	0.54
Oxidation corrosion test, 168 hr. at 250° F.—wt. loss, mg./cm.²:	
Cu	0.08
Mg	0.02
Fe	0.02
Cd	3.81
Al	0.01
Per cent increase in viscosity at 100° F.	52
Acid Neut. No. after use	15.9
4 ball wear (7 kg., 80° C.)	0.21
Pipe cleaner flash	17
Pipe cleaner fire	21

AROMATIC AMINES

As Table 5 above shows, the addition of the calcium salt provided a composition which showed acceptable properties with respect to corrosion except for cadmium. Moreover, there was a substantial increase in viscosity of the composition after the oxidation corrosion test. It was found that the addition of an epoxide compound or an aromatic amine to these compositions eliminates the cadmium corrosion and reduces the increase in viscosity during the oxidation corrosion test to a remarkable extent. Table VI which follows shows typical results in this respect.

Table VI

Trioctylphosphate, wt. percent	59.8	84.6
Bright Stock, wt. percent	38.2	13.4
Calcium Salt, wt. percent	1.0	1.0
Phenyl alpha naphthylamine, wt. percent	1	1
Viscosity Cs. 100° F	33.51	13.23
Viscosity Cs. 210° F	5.76	3.12
Viscosity Index	123	107
Pour Point, °F	−45	−65
Acid Neut. No		
MIL-O-5606 Specification—Oxidation Corrosion 168 hr. at 250° F.—Weight Loss, mg./cm.²:		
Cu	0.06	.03
Mg	0	.02
Fe	0	0
Cd	0.06	.02
Al	0	.01
Percent Increase in Viscosity at 100° F	8	0.3
Acid Neut. No. after use	0.81	.11

The organic amines useful in this invention preferably contain at least 10 carbon atoms. They may be either mono-cyclic or polycyclic aromatic amines. The naphthylamines are preferred and include primary, secondary, or tertiary amines such as phenyl alpha naphthylamine, phenyl beta naphthylamine, diphenyl naphthylamine, and benzylphenyl naphthylamine. Mono-cyclic aromatic amines include especially the polyamino phenylene compounds such as the paraphenylene diamines, e. g. 2,4-diamino toluene and N,N'-dibutylparaphenylene diamine. The alkylated phenyl amines are also useful such as 1-isopropyl-4-amino benzene, 1-hexyl - 3 - amino benzene, 1 - amino - 2 - methyl-6-ethylbenzene and 1-amino-2,4-diethylbenzene.

In order to provide an effective synergistic result with the metallic salts described hereinbefore, the aromatic amines should be present in an amount between about 0.25% and about 5% by weight of the total composition. In the absence of the metallic salts described above, the aromatic amines have proved to be unsatisfactory for the purpose of stabilizing these compositions against oxidation corrosion. On the other hand, as described above, the metallic salts do not fully protect cadmium against corrosion and permit a substantial increase in viscosity upon exposure to oxygen. However, as the data contained in Table VI indicate, combinations of these two additives provide substantially complete protection in these respects.

The pipe cleaner flammability test is made as follows: A pipe cleaner, reduced to 4¼ inches in length, is saturated with fluid to be tested, the excess drained and the cleaner inserted in a metal holder. It is then cycled at 36 R. P. M. between two electric hot plates mounted horizontally one-half inch apart with ceramic grids over the open coil heaters. The temperature between the grids varies between 760 and 710° C., dropping during the test. The number of passes necessary to cause initial flash and continuous fire are recorded.

In addition to the ingredients described hereinbefore, these compositions may contain other lubricating oil and hydraulic fluid components or additives. In certain compositions wherein the proportion of bright stock is above about 35% and the composition is to be used at relatively low temperatures, it is desirable to incorporate therein one or more pour point depressants. The most satisfactory type of material comprises polymerized esters of the acrylic acid series. These include especially the esters of methacrylic acid and of acrylic acid. The former are available as commercial products and are sold under the trade name "Acryloid." The esters to be used should have molecular weights from about 5,000 to about 25,000, which will be understood to be an average figure for the mixture of polymers normally present. The acids are esterified with aliphatic alcohols having from 2 to 15 carbon atoms and the polymers may be homopolymers of a single ester or may be copolymers of a mixture of such esters. The term "polymerized esters" will be understood to include both of these types.

Another type of pour point depressant suitable for use in the present compositions includes the condensation products of high molecular weight paraffins and polycyclic aromatics such as the condensation products produced by condensing chlorinated paraffin wax and naphthalene.

I claim as my invention:

1. A composition comprising essentially from about 50% to about 92.5% by weight of a normally liquid trialkyl phosphate said ester having at least 18 carbon atoms per molecule, from about 7.5% to about 60% by weight of a mineral oil bright stock having a viscosity of between about 1250 and 11,000 SUS at 100° F., said oil containing less than about 15% by weight of aromatic hydrocarbons and said composition containing from about 0.25% to about 5% by weight of an alkaline earth metal salt of a condensation product of formaldehyde with alkyl phenols the alkyl groups thereof containing from 4 to 12 carbon atoms, and 0.25–5% by weight of a naphthylamine.

2. A hydraulic fluid composition comprising the following ingredients in the stated proportions:

	Per cent
Trioctylphosphate	59.8
Mineral oil bright stock	38.2
Phenyl alpha-naphthylamine	1
Calcium salt of the condensation product of formaldehyde with amyl phenol	1

said mineral oil bright stock having a viscosity of between about 1250 and 11,000 SUS at 100° F. and containing less than 15% by weight of aromatic hydrocarbons.

3. A hydraulic fluid composition comprising essentially the following ingredients in the stated proportions:

	Per cent by weight
Trioctyl phosphate	50–70
Mineral oil bright stock	30–50
Phenyl alpha naphthylamine	0.25–5
Calcium salt of the condensation product of formaldehyde with amyl phenol	0.25–5

said mineral oil bright stock having a viscosity of between about 1250 and 11,000 SUS at 100° F. and containing less than about 15% by weight of aromatic hydrocarbons.

4. A hydraulic fluid composition comprising essentially the following ingredients in the stated proportions:

	Per cent by weight
Trialkyl phosphate, each alkyl radical thereof containing from 6 to 12 carbon atoms	50–70
Mineral oil bright stock	30–50
Phenyl alpha naphthylamine	0.25–5
Calcium salt of the condensation product of formaldehyde with amyl phenol	0.25–5

said mineral oil bright stock having a viscosity of between about 1250 and 11,000 SUS at 100° F. and containing less than about 15% by weight of aromatic hydrocarbons.

5. A hydraulic fluid composition comprising essentially the following ingredients in the stated proportions:

	Per cent by weight
Trialkyl phosphate, each alkyl radical thereof containing from 6 to 12 carbon atoms	50–70
Mineral oil bright stock	30–50
A naphthylamine	0.25–5
Calcium salt of the condensation product of formaldehyde with amyl phenol	0.25–5

said mineral oil bright stock having a viscosity of between about 1250 and 11,000 SUS at 100° F. and containing less than about 15% by weight of aromatic hydrocarbons.

6. A hydraulic fluid composition comprising essentially the following ingredients in the stated proportions:

	Per cent by weight
Trialkyl phosphate, each alkyl radical thereof containing from 6 to 12 carbon atoms	50–70
Mineral oil bright stock	30–50
Phenyl alpha naphthylamine	0.25–5
Calcium salt of the condensation product of formaldehyde with alkyl phenol, each alkyl radical thereof containing from 4 to 12 carbon atoms	0.25–5

said mineral oil bright stock having a viscosity of between about 1250 and 11,000 SUS at 100° F. and containing less than about 15% by weight of aromatic hydrocarbons.

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