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POLYPHENYL ETHER BLENDS

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This invention relates to functional fluids, and more particularly, provides novel functional fluids comprising mixtures of ester base fluids and polyphenyl ethers.

Use of functional fluids as lubricants for aircraft engines such as jet engines requires fluidity at low temperatures. The lubricant must be at least fluid enough to permit free movement of engine parts in starting up at ambient outdoor temperatures, down to at least, say, 0° F. On the other hand, high-speed engines such as jet engines are designed for operating temperatures as high as about 500° F., and the lubricant must be reasonably stable at operating temperatures. A minimum operating life of 50 to 100 hours should be obtainable before the lubricant has deteriorated to such an extent that it must be drained and replaced with fresh material.

The polyphenyl ether fluids have been found to be well adapted for use as functional fluids in applications requiring high temperature stability. They have unusually good thermal and oxidative stability. These fluids, moreover, have superior lubricating ability and resistance to foaming.

The polyphenyl ethers have a very wide liquid range, remaining in the liquid phase at temperatures from below 100° F. up to as high as 800° F. or above. The meta-linked variety have a particularly wide liquid range, and it has been found that a mixture of about 65% (by weight) m - bis(m-phenoxyphenoxy)benzene, 30% m-[(m-phenoxyphenoxy)(p-phenoxyphenoxy)]benzene and 5% m-bis(p-phenoxyphenoxy)benzene provides a composition which is liquid at below ordinary room temperature, while retaining thermal stability to above 800° F. However, the pour point of this mixture, at which its viscosity becomes above 500,000 centistokes, is about 40° F., so that use of this material itself where engine cold starts are required is impractical.

It is an object of this invention to provide improved functional fluid compositions.

A particular object of this invention is to provide functional fluid compositions comprising polyphenyl ether base fluids having an improved liquid operating temperature range.

These and other objects will become evident upon consideration of the following specification and claims.

It has now been found that blends of polyphenyl ether and ester lubricant base fluids provide functional fluid compositons having an advantageous liquid range and which, particularly when combined with antioxidant additives as set forth hereinafter, also possess unusual high temperature oxidative stability. These functional fluid compositions are particularly adapted for use as lubricants in environments such as jet engines, requiring fluidity in the liquid phase combined with oxidative stability over a range such as from 0° F. to 500° F.

The polyphenyl ethers are not generally miscible with other base fluids: they do not dissolve more than about 5% by weight mineral oil, for example. Attempts to blend silicones with the phenyl ether base fluids have

shown that only a few of this class of fluids are miscible with the polyphenyl ethers, and then to a limited extent. However, it has been found that the polyphenyl ethers can be combined with other oxygenated carbonaceous base fluids to provide homogeneous fluids having advantageous properties.

Blending of ester base fluids with the polyphenyl ethers has been discovered to result in an unexpectedly steep reduction of the viscosity of the ethers. The viscosities of the blends are not the arithmetical average of the components, and indeed, reduction of the ether viscosity produced by introduction of the ester is even greater than can be attributed to a logarithmic effect. Thus, blends can be produced with the fluidity range needed for lubricant use, where the engine must be able to make a cold start and yet operate at elevated temperatures, employing ether: ester weight ratios in the range of from 25:75 to 75:25. These blends, containing a substantial proportion of the polyphenyl ethers, have desirably enhanced high temperature oxidative stability as compared to the ester components thereof. The percentage viscosity increase on exposure of the blends to oxidative conditions at elevated temperatures is sufficiently diminished to make the blends useful as functional fluids at operating temperatures where the ester itself cannot be used.

Especially advantageous high temperature oxidative stability is exhibited by blends of 25 to 75 weight percent polyphenyl ethers with 75 to 25 weight percent neopentyl polyol ester base fluids. These blends remain clear and free of objectionable solids during oxidative decomposition. Moreover, these blends are found to be unexpectedly responsive to certain anti-oxidant additives.

Temperature has been shown to be critical to the high temperature oxidative stability of neopentyl polyol base fluids. At 425° F., an inhibited trimethylolpropane ester is degraded only slightly by exposure to an air flow as high as 96 liters per hours (Gunderson et al., eds, "Synthetic Lubricants," Reinhold, 1962, p. 395). Att 500° F., however, the same fluid almost doubles in viscosity within 24 hours at a 5 liter per hour air flow rate.

The presently provided blends of neopentyl polyol esters with polyphenyl ethers have been found to exhibit a unique and pronounced oxidative stability increase upon combination with an (alkanedionato) cobalt coordination compound. The 500° F. oxidative stability of the blends combined with such cobalt compounds is markedly superior to that of a blend containing the inhibitor used in the ester providing the above-stated results. Unexpectedly, other metal pentanedionates do not exhibit such antioxidant activity, and indeed, exert a pro-oxidant effect in the blends.

Furthermore, it has been found that combinations of a cobalt alkanedionate with an aromatic amine compound are effective antioxidants for the stated blends. The useful amines include polyaryl amines and polyarylidene polyamines containing at least two benzene nuclei.

Thus, in accordance with the present invention, there are provided compositions which not only have the fluidity at 0° F. and below that the polyphenyl ethers lack, but also the oxidative stability at 500° F. that the neopentyl polyol esters lack, and which are uniquely adapted as lubricants for jet engine systems requiring ability to operate from a cold start up to running temperatures of about 500° F.

The polyphenyl ethers employed in the compositions of this invention have from 3 to 7 benzene rings and from 1 to 6 oxygen atoms, with the stated oxygen atoms joining the benzene rings in chains as ether linkages. One or more of the benzene rings in these polyphenyl ethers may be hydrocarbyl substituted. The hydrocarbyl substituents, for thermal stability, must be free of CH_2 and aliphatic CH, so that preferred aliphatic substituents are lower saturated hydrocarbon radicals (1 to 6 carbon atoms) like methyl and tert-butyl, and preferred aromatic substituents are aryl radicals like phenyl, tolyl, t-butylphenyl and α-cumyl. In the latter case, the benzene ring supplied in the hydrocarbyl substituent contributes to the total number of benzene rings in the molecule. Polyphenyl ethers consisting exclusively of chains of from 3 to 7 benzene rings with at least one oxygen atom joining the stated benzene rings in the chains as an ether linkage have particularly desirable thermal stability.

Exemplary of the polyphenyl ethers containing aliphatic carbon which are suitable for high temperature base fluids are 3-ring polyphenyl ethers like 1-(p-methylphenoxy)-4-phenoxybenzene and 2,4-diphenoxy-1-methylbenzene, 4-ring polyphenyl ethers like bis[p-(p-methylphenoxy)phenyl] ether and bis[p-(p-tert-butylphenoxy)phenyl] ether, and so forth.

Polyphenyl ethers consisting exclusively of benzene rings and including ether oxygen atoms linking said rings are exemplified by the triphenoxy benzenes and aryl-substituted polyphenyl ethers such as biphenylyl phenoxyphenyl ether, biphenylyloxyphenyl phenoxyphenyl ether, biphenylyl ether, dibiphenylyloxybenzene, bis(biphenylyloxyphenyl) ether, and the like.

A preferred class of the polyphenyl ethers are those consisting of benzene rings joined in a chain by oxygen atoms as ether linkages between each ring, of the formula $C_6H_5O—(C_6H_4O—)_n—C_6H_5$ where n is an integer of from 1 to 5.

Examples of the polyphenyl ethers contemplated in this class are the bis(phenoxyphenyl) ethers (4 benzene rings joined in a chain by 3 oxygen atoms), illustrative of which is bis(m-phenoxyphenyl) ether. The bis(phenoxyphenoxy) benzenes are particularly valuable in the present connection. Illustrative of these are m-bis(m-phenoxyphenoxy)benzene, m-bis(p-phenoxyphenoxy) benzene, o-bis(o-phenoxyphenoxy)benzene, and so forth. Further, the polyphenyl ethers contemplated herein include the bis(phenoxyphenoxyphenyl) ethers such as bis[m-(m-phenoxyphenoxy)phenyl] ether, bis[p-(p-phenoxyphenoxy)phenyl] ether, and m-(m-phenoxyphenoxy) phenyl m-(o-phenoxyphenoxy)phenyl ether, and the bis(phenoxyphenoxyphenoxy)benzenes such as m-bis[m-(m-phenoxyphenoxy)phenoxy]benzene, p-bis[p-(m-phenoxyphenoxy)phenoxy]benzene and m-bis[m-(p-phenoxyphenoxy)phenoxy]benzene.

The preferred polyphenyl ethers are those having all their ether linkages in the meta-positions since the all-meta-linked ethers are particularly advantageous because of their wide liquid range and high thermal stability. However, mixtures of the polyphenyl ethers, either isomeric mixtures or mixtures of homologous ethers, can also advantageously be used in some applications, especially where particular properties such as lower solidification points are required. Mixtures of polyphenyl ethers in which the non-terminal phenylene rings are linked through oxygen atoms in the meta and para positions have been found to be particularly suitable to provide compositions with wide liquid ranges. Of the mixtures having only meta and para linkages, a preferred polyphenyl ether mixture of this invention is the mixture of bis(phenoxyphenoxy)benzenes wherein the non-terminal phenylene rings are linked through oxygen atoms in the meta and para position, and composed by weight of about 65% m-bis(m-phenoxyphenoxy)benzene, 30% m[(m-phenoxyphenoxy)(p-phenoxyphenoxy)]benzene and 5% m-bis(p-phenoxyphenoxy)benzene. Such a mixture solidifies at below room temperature (that is, below about 70° F.) whereas the three components solidify individually at temperatures above normal room temperatures.

The aforesaid polyphenyl ethers can be obtained by known procedures such as, for example, the Ullmann ether synthesis, which broadly relates to ether-forming reactions wherein alkali metal phenoxides such as sodium and potassium phenoxide are reacted with aromatic halides such as bromobenzene in the presence of a copper catalyst such as metallic copper, copper hydroxides, or copper salts.

The high temperature, oxygenated carbonaceous base fluids employed in the compositions of this invention will also comprise a synthetic ester base fluid. These are fluids of lubricating viscosity and thermally stable to at least about 400° F., which are esters of alcohols containing at least 4 carbon atoms and which generally contain more than one ester group. They may be esters of polyhydric alcohols, of polybasic acids, or both.

Ester fluids with particularly advantageous low temperature viscosity properties, which flow readily at temperatures as low as —30° F., are provided by the diesters of dibasic acids. Ester lubricants of the dibasic acid ester type are illustrated by diesters of long chain dicarboxylic acids like azelaic acid with long-chain branched primary alcohols of the C_4 to C_{10} range. The synthetic ester lubricants also frequently include the esters of long chain monobasic acids such as pelargonic acid with glycols such as polyethylene glycols. Complex esters are also formed by linking dibasic acid half esters through a glycol such as dipropylene glycol, a polyethylene glycol of 200 molecular weight, and so forth. Permutation and combination of these methods of forming polyester type lubricant fluids have been reported to be valuable and also, it is common practice to achieve desired properties in the ultimate base fluid by blending different polyester products. Simple esters providing suitable fluids can be exemplified, for example, by bis(2-methylbutyl) sebacate, bis(1-methyl-4-ethyloctyl) sebacate, bis(2-ethylhexyl) sebacate, dipropylene glycol dipelargonate, the diesters of acids such as sebacic, azelaic and adipic acid with complex C_8–C_{10} primary branched chain alcohols such as those produced by the oxo process, polyethylene glycol 200 bis(2-ethylhexyl sebacate), diisoamyl adipate, 1,6-hexamethylene glycol di(2-ethylhexanoate), bis(dimethylamyl) azelate and so forth.

Ester fluids with particularly good high temperature oxidation resistance are provided by neopentyl polyol esters. The alcohols from which these esters are derived have the carbon structure of neopentane, with a central carbon atom surrounded by 4 substituent carbon atoms. Included in the neopentyl polyols are neopentyl glycol, trimethylolethane, trimethylolpropane and pentaerythritol. Generally, the base fluids comprising neopentyl polyol esters are the esters with monocarboxylic acids. Such esters are generally more oxidatively and thermally stable than the dibasic acid esters. The useful esters of the neopentyl polyols include, for example, the esters of trimethylol propane, neopentyl glycol and pentaerythritol with normal, branched chain and mixed acids having chain lengths varying from C_6 to C_{12}. Thus, an illustrative series of esters are trimethylolpropane tri-n-pelargonate, trimethylolpropane tricaprate, trimethylolpropane tricaprylate, the trimethylolpropane triester of mixed octanoates, and the like.

For further description of still other ester fluids adapted for use as lubricant base stocks and useful in the provision of the blends of this invention, reference may be made, for example, to the discussion in Gunderson et al. "Synthetic Lubricants" (Reinhold, 1962).

The polyphenyl ether blends of the present invention will consist of a blend of at least one polyphenyl ether and at least one ester lubricant base fluid, with the polyphenyl ether component providing from about 25 to 75 weight percent of the total. These blends will have a pour point at least as low as about 0° F.; desirably, they will have a pour point well below 0° F., and a viscosity of below about 25,000 centistokes at 0° F.

Illustrative of the fluid blends of this invention are, for example, blends of polyphenyl ethers with diesters. Preferred compositions of this nature include blends of bis(phenoxyphenoxy)benzenes with alkanedicarboxylic acid diesters of alkanols of the formula

$$R_1OOC—R_2—COOR_3$$

wherein each of R_1, R_2 and R_3 are saturated aliphatic hydrocarbon of from 4 to 12 C atoms. Thus for example, such blends are illustrated by blends in which 25 to 75 weight percent of the total is a bis(phenoxyphenoxy)benzene and the remainder is a dialkyl alkanedicarboxylate such as bis(2-ethylhexyl) sebacate, bis(2-ethylhexyl) azelate, bis(1-methylcyclohexyl) sebacate, di-C_8-oxo azelate and di-C_{10}-oxo azelate (where the oxo alcohols are mixtures of branched chain alcohols made by the oxo process, C_8 oxo alcohol consisting chiefly of a mixture of 3,4-, 3,5-, and 4,5-dimethyl-1-hexanol, for example). Other blends including diesters can be provided, for example, by combining one or more bis(phenoxyphenoxy)benzenes with a fluoroalkyl diester such as 1,1-H-perfluoroheptyl sebacate, with a polyalkylene glycol ester such as dipropylene glycol dipelargonate, and so forth. Still other useful blends may be prepared by combining polyphenyl ethers such as trisphenoxybenzenes, bis(phenoxyphenyl) ethers, diphenoxybenzenes and the like with ethers such as bis(1-ethylpropyl) adipate, bis(1,3-dimethylbutyl) sebacate, di(2-ethylhexyl) sebacate and the like, or with other combinations of the polyphenyl ethers and diester lubricant base stocks such as those mentioned above.

Further illustrative of the fluid blends of base stocks provided by this invention is the especially preferred class of blends of polyphenyl ethers with neopentyl polyesters. Exemplary of this class are blends of bis(phenoxyphenyl) ethers and of bis(phenoxyphenoxy)benzenes, preferably including the ethers with meta-oriented substituents, with trimethylolpropane esters such as the tri-n-heptanoate and trineoheptanoate and with pentaerythritol esters such as the tetracaprate and tetracaproate esters, and so forth. Still other illustrative blends are provided by combinations of polyphenyl ethers such as 1-(p-α-cumylphenoxy)-4-phenoxybenzene, mixed bis(phenoxyphenoxy)benzenes, and so forth, with neopentyl glycol n-heptanoate, pentaerythritol tetraester with mixed nonanoic acids and the like, as well as by other combinations of the polyphenyl ethers with neopentyl polyol esters as discussed above. Also, it is to be appreciated that mixtures of different polyphenyl ethers, diesters and neopentyl polyol esters are in the scope of the blend compositions of this invention.

Formulated compositions wherein an antioxidant additive is combined with the stated base stock blends are provided in accordance with the present invention, wherein an adjuvant amount of an (alkanedionato) cobalt coordination compound is combined with polyphenyl ether/synthetic ester base fluid blend of the above-discussed nature.

The presently useful cobalt coordination compounds include the cobaltous and cobaltic 1,3-propanedionates (alkanedionates with beta-positioned oxo groups) wherein substituents of the propanedione carbon chain are hydrocarbon free of aliphatic (olefinic and acetylenic) unsaturation, and the dione may contain from 5 to 15 carbon atoms. Thus for example, illustrative cobalt compounds of the stated nature are bis(2,4-pentanedionato) cobalt, tris(2,4 - pentanedionato) cobalt, tris(2 - ethyl - 1-phenyl-1,3-hexanedionato) cobalt, tris(2,4-hexanedionato) cobalt, bis(2,4-hexanedionato) cobalt, tris(5,5-dimethyl-2,4-hexanedionato) cobalt, tris(5-methyl-2,4-hexanedionato) cobalt, tris(3-benzyl-2,4-pentanedionato) cobalt, bis(2-ethyl-1-phenyl-1,3-butanedionato) cobalt, tris(2-methyl-1-phenyl-1,3-butanedionato) cobalt, tris(1-naphthyl-1,3-butanedionato) cobalt, tris(1-phenyl-1,3-butanedionato) cobalt, tris(1,3-diphenyl-1,3-propanedionato) cobalt, and the like.

The antioxidant additive employed in the formulated lubricants of this invention may consist of the cobalt alkanedionate alone or in combination with further oxidation-suppressing additives. It has been found that particularly effective suppression of the oxidative degradation of the present base stock blends is produced by combinations of aromatic amines with the cobalt alkanedionate compounds.

By an aromatic amine is meant an amine including a benzene ring. For the present purposes, useful amines contain at least two benzene nuclei, which may be either phenyl radicals or part of a fused ring system such as naphthyl. Presently useful amines include arylamines and arylidene amines wherein the benzene nuclei are attached to the amine nitrogen atoms either directly by a ring carbon atom or through a single aliphatic carbon atom. The aromatic amines contemplated herein are free of aliphatic (olefinic and aetylenic) unsaturation, contain from 12 to 36 carbon atoms, and consist of hydrocarbon radicals and amino nitrogen atoms, which may or may not have oxy (oxygen joined to atoms selected from C and H) radicals as substituents. Generally the presently contemplated amines will include from 1 to 4 N and from 0 to 3 O atoms.

Illustrative of presently useful aromatic amines are aryl amines such as naphthylamine (α or β), naphthylenediamine (1,2- 1,5- 1,8-), N-methyl-β-naphthylamine, benzidine, 2,4′-diaminobiphenyl, 2-aminobiphenyl, 4-aminobiphenyl, diphenylamine, 4-aminodiphenylamine, N-phenylphenylenediamine, N-ethyl-α-naphthylamine, 2,4-diaminodiphenylamine, 1,2-diphenylethylenediamine, N-benzylaniline, methylenedianiline, 1-aminoanthracene, 1-aminophenanthrene, di-p-tolylamine, 4-dimethylaminodiphenylamine, N,N′-diphenylethylenediamine, o-ditoluidine(3,3′-diamino - 4,4′ - dimethylbiphenyl), N - phenyl - α - naphthylamine, N-phenyl-β-naphthylamine, N-cyclohexyl-α-naphthylamine (or β), N-p-tolyl-β-naphthylamine, triphenylamine, N,N′ - diphenyl - p - phenylenediamine, di-α-naphthylamine, di-β-naphthylamine, dibiphenylylamine, N,N′-diphenylbenzidine, p-aminophenyltriphenylmethane, N,N′, - dinaphthylmethylenediamine, N,N′ - dinaphthyl-p-phenylenediamine, N-[(1-aminocyclohexyl)methyl]-N′-phenyl-p-phenylenediamine, and so forth.

Exemplary of presently useful arylidene amines are N,N′-dibenzylidene-p-phenylenediamine, N,N′ - bis(2,3-dimethylbenzylidene)-p-phenylenediamine, N,N′ - bis(2-hydroxybenzylidene)-p-phenylenediamine, N,N′ - bis(2-ethoxybenzylidene)-p-phenylenediamine, N,N′ - bis(2-hydroxybenzylidene)ethylenediamine, N,N′ - bis(2 - hydroxybenzylidene)-1,2-propylenediamine, N,N′ - bis(2-hydroxybenzylidene)-1,3-propylenediamine, N,N′ - bis(3-ethoxy - 4 - hydroxybenzylidene)-1,2-propylenediamine, N,N′ - bis(2-hydroxy-4-methylbenzylidene)-p-phenylenediamine, N-3-methylbenzylidene-3-octylaniline, N-2-hydroxybenzylidene-4-hexadecylaniline, N′,N-bis(3,4-methylenedioxybenzylidene)-p-phenylenediamine, N,N′-bis(2,3-dimethoxybenzylidene)-p-phenylenediamine, N,N′ - bis(2-methoxybenzylidene)-p-phenylenediamine, N,N′ - bis(2-hydroxybenzylidene)-o-phenylenediamine, N,N′ - bis(3 - methoxy-4-hydroxybenzylidene)-p-phenylenediamine, N,N′ - bis(3-ethoxy-4-hydroxybenzylidene)-p-phenylenediamine, N-(3-ethoxy-4-hydroxybenzylidene)-4-dodecylaniline, N,N′ - bis(4-phenoxybenzylidene)-p-phenylenediamine, N,N′ - dibenzylidene-1,2 - diphenylethylenediamine, and the like.

The antioxidant compounds are combined with the base fluid to the extent of, generally, between about 0.01% and 10%, individually or jointly, by weight of the fluid.

Particular effective amounts depend on the nature of the individual additive and of the base fluid.

It will be appreciated that the present compositions may additionally include any of a wide variety of further additives. For example, the base fluids may be combined with lubricity improvers effective to increase load-carrying ability, decrease wear, or both, with viscosity index improvers such as polymethacrylate alkyl esters, with detersives and dispersants, and so forth.

The invention is illustrated but not limited by the following examples, in which the tests employed to determine the reported adjuvant effects of the additive compounds when employed with the polyphenyl ether lubricant base fluid are conducted as follows:

For determination of the antioxidant effect of the present additive compounds, air is bubbled through heated samples of the base fluids and base fluids plus additives. The percent change in (100° F.) viscosity from before to after oxidation is an index of anti-oxidant activity. The conditions employed are temperatures of 500° and a flow rate of 1 liter of air per hour. Samples are run in the presence and absence of metal wires (silver, copper, aluminum, stainless steel) as a check on the effect of such metals on the oxidation rate.

Example 1

This example illustrates the blends of this invention, and viscosity properties of the blends.

The polyphenyl ether base stock referred to in the following discussion is a bis(phenoxyphenoxy)benzene mixture of the composition

65% m-bis(m-phenoxyphenoxy)benzene
30% m-[(m-phenoxyphenoxy)(p-phenoxyphenoxy)] benzene
5% m-bis(p-phenoxyphenoxy)benzene.

This fluid is liquid at room temperature, has a viscosity of about 350 centistokes (cs.) at 100° F., and has a pour point (viscosity above 500,000 cs.) of 40° F.

Measurements of viscosity of blends of this ether base stock with bis(2-ethylhexyl)sebacate give the following results:

Percent Ester	Viscosity, cs.	
	Low Temp.	100° F.
None		350
35	14,000/0° F.	53
60	13,000/−30° F.	26
100	838/−30° F.	13

A blend of bis(1-methylcyclohexyl) sebacate and the bis(phenoxyphenoxy)benzene mixture described above, of which 55% is the said bis(phenoxyphenoxy)benzene mixture, has a 100° F. viscosity of 105 cs., and a blend of 45% resorcinyl dineoheptanoate with 55% of the stated bis(phenoxyphenoxy)benzenes mixture has a 100° F. viscosity of 73 cs.

Example 2

This example further ilustrates the blends of this invention, exemplifying blends including a neopentyl polyol ester.

The mixture of bis(phenoxyphenoxy)benzenes described in the above example is combined with pentaerythritol tetracaprate (identified herein as PE–TCA), pentaerythritol tetracaproate (identified herein as PE–TCO), trimethylolpropane trienanthate (identified below as C–TMP) and with another, similar trimethoylol triester with mixed alkanecarboxylic acids of about C_7 chain length (identified herein below as HN–TMP), to provide base stock blends.

The viscosities of these blends are measured, and the blends are subjected to the above-described oxidation test,

conducted by exposing the base stocks to an air flow rate of 1 liter per hour for 24 hours at 500° F. in the presence of metal (Al, Cu. Ag, and Fe) wires.

Results are tabulated in the following table:

Ester, percent	Viscosity, cs.		Percent Change Viscosity in Oxidation Test
	0° F.	100° F.	
None		350	0
C–TMP, 100%		15	200
C–TMP, 50%	6,300	50	
C–TMP, 45%	11,000	50	100
HN–TMP, 100%		14	150
HN–TMP, 45%	8,800	47	100
PE–TCO, 100%		25	300
PE–TCO, 50%	12,000	51	
PE–TCO, 55%	6,900	45	100
PE–TCA, 100%		40	200
PE–TCA, 70%		51	125

Example 3

This example illustrates still another embodiment of the base stock blends of this invention.

Blends are prepared by combining bis(m-phenoxyphenyl) ether with the trimethylolpropane trienanthate identified in Example 2 as C–TMP. The composition consisting of 80% ether and 20% ester has a 0° F. viscosity of 22,000 cs., and a 100° F. viscosity of 38 cs.; in the proportion of 70% ether and 30% ester, the base stock blend has a 0° F. viscosity of 6800 cs. and a 100° F. viscosity of 32 cs.

Example 4

This example illustrates still other blend compositions of this invention, produced by combining three different base stocks.

Blends having a 100° F. viscosity of 39 cs. are prepared by combining pentaerythritol tetracaprate, the trimethylolpropane trienanthate ester identified above as the C–TMP ester, and the mixture of bis(phenoxyphenoxy)benzenes described in Example 1, in the following weight proportions:

34 :29 :37
37.5:28.1:34.4
39.4:27.3:33.3

Employing the oxidation conditions stated in Example 3, it is found that these blends are approximately doubled in viscosity at the end of the test.

Example 5

This example illustrates the formulated blended base stock compositions of the invention.

Cobaltous bis- and cobaltic tris(2,4-pentanedionate) are respectively combined, in a concentration of up to one gram per 100 grams of base fluid, with base stock blends prepared and identified as described in Example 3, which are neopentyl polyol ester blends with a bis(phenoxyphenoxy)benzene mixture. These compositions containing the coordination compounds are subjected to the 500° F. oxidation test described above. The viscosity increases are substantially lower than those of the base stocks, as appears from the data shown in the following table:

Ester, percent	Pentanedionato Co compound	100° F. Viscosity, cs.			Evap., percent
		Before test	After test	Percent change	
C–TMP, 45%	tris-	47	53	13	5.0
C–TMP, 45%	bis-	50	65	30	1.0
HN–TMP, 45%	bis-	48	61	27	7.6

In another series of runs, made with compositions including base stocks blends prepared and identified as described in Example 3, and 1 g./100 g. base stock of freshly prepared cobalt 2,4-pentanedionate, results obtained are as follows:

Ester, percent	Pentane-dionato Co compound	100° F. Viscosity, cs.			Evap., percent
		Before test	After test	Percent change	
C–TMP, 45%	tris-	52	56	8	3.0
PE–TGA, 70%	tris-	56	61	11	2.0

Under the same conditions, the blend containing 45% C–TMP ester combined with 1% of 5-phenyl-10,10-diphenylphenazasilane has an initial viscosity of 50 cs., and an after-test viscosity of 76 cs., which is an increase of 52% in 24 hours, with an evaporation loss of 5.0%. The TMP ester blends combined with the 1,3-pentanedionato sodium, chromium, titanium and zinc chelate compounds form heavy deposits in 24 hours, amounting to as much as 90% of the weight of the sample.

Example 6

This example illustrates compositions having enhanced oxidation resistance produced by combining a blended base stock with a combination of a cobalt chelate and an aromatic amine.

The blend of 45% of the ester base fluid identified as C–TMP and 55% of mixed bis(phenoxyphenoxy)benzenes described in Example 3 is combined with (2,4-pentanedionato) cobalt compounds and aromatic amines as indicated below, and the resulting compositions subjected to the 500° F. oxidation test described previously, with results as shown in the following table.

Co, percent [1]	Aromatic Amine, percent	Change, percent [2]
Bis-, 0.27%	N-[(1-aminocyclohexyl)methyl]-N′-phenyl-p-phenylenediamine, 0.5%.	[3] 13
Tris-, 1%	Diphenylamine, 2%	26
Bis-, 1%	N,N′-bis(2-hydroxybenzylidene)-1,2-propylenediamine, 1%.	11
Bis-, 0.5%	N,N′-bis(2-hydroxybenzylidene)-1,2-propylenediamine, 0.75%.	9
Tris-, 1%	N,N′-bis(2-hydroxybenzylidene)-1,2-propylenediamine, 1%.	15

[1] Bis: bis(2,4-pentanedionato) cobalt. Tris: tris(2,4-pentanedionato) cobalt. Percent: weight percent of weight of base fluid.
[2] Percent change in 100° F. viscosity, cs.
[3] Average of multiply determinations.

While the invention has been described with reference to various particular preferred embodiments thereof, it is to be appreciated that modifications and variations can be made without departing from the scope of the invention, which is limited only as described in the appended claims.

What is claimed is:

1. A functional fluid composition having a pour point below about 0° F., consisting essentially of a base stock blend of at least one polyphenyl ether and at least one synthetic ester base fluid, in which the polyphenyl ether constituent provides from 25 to 75 weight percent of the total, and the said synthetic ester base fluid constituent is a fluid of lubricating viscosity thermally stable to at least about 400° F., said ester being the ester of an alcohol containing at least 4 carbon atoms, and a 1,3-propanedionato cobalt compound, in an amount sufficient to increase the oxidative stability of said base stock blend.

2. A functional fluid composition having a pour point below about 0° F., consisting essentially of a base stock blend of a polyphenyl ether consisting of a chain of benzene rings including at least one oxygen atoms as an ether linkage between said benzene rings and a neopentyl polyol ester, wherein said polyphenyl ether provides from 25 to 75 weight percent of the total, an aromatic amine containing at least two benzene nuclei, in an amount of from about 0.01% to 10% by weight of said base stock blend, and a 1,3-propanedionato cobalt compound, in an amount of from about 0.01% to 10% by weight of said base stock blend, the combined amounts of said aromatic amine and said 1,3-propanedionato cobalt compound being sufficient to increase the oxidative stability of said base stock blend.

3. A functional fluid composition having a pour point below about 0° F., consisting essentially of a base fluid blend of a polyphenyl ether consisting of a chain of from 3 to 7 benzene rings and oxygen atoms as ether linkages between each ring in the chain, and a trimethylolpropane trialkanoate ester, wherein said polyphenyl ether provides from 25 to 75 percent of the weight of the total, and a 1,3-propanedionato cobalt compound, in an amount sufficent to increase the oxidative stability of said base stock blend.

4. The composition of claim 3 wherein said 1,3-propanedionato cobalt compound is a (2,4-pentanedionato) cobalt compound.

5. A functional fluid composition having a pour point below about 0° F., consisting essentially of a base fluid blend of a polyphenyl ether consisting of a chain of from 3 to 7 benzene rings and oxygen atoms as ether linkages between each ring in the chain, and a trimethylolpropane trialkanoate ester, wherein said polyphenyl ether provides from 25 to 75 percent of the weight of the total, from about 0.01% to 10%, by weight of said base fluid blend, of a 1,3-propanedionato cobalt compound, and from about 0.01% to 10%, by weight of said base fluid blend, of an aromatic amine containing at least two benzene nuclei, the combined amounts of said 1,3-propanedionato cobalt compound and said aromatic amine being sufficient to increase the oxidative stability of said base stock blend.

6. A functional fluid composition having a pour point below about 0° F., consisting essentially of a base fluid blend of a mixture of bis(phenoxyphenoxy)benzenes and trimethylolpropane trienanthate, wherein said mixture of bis(phenoxyphenoxy)benzenes provides from 25 to 75 percent of the weight of the total, and a 1,3-propanedionato cobalt compound in an amount sufficient to increase the oxidative stability of said base fluid blend.

7. The composition of claim 6 in which said cobalt compound is bis(2,4-pentanedionato) cobalt (II).

8. The composition of claim 6 in which said cobalt compound is tris(2,4-pentanedionato) cobalt (III).

9. A functional fluid composition having a pour point below about 0° F., consisting essentially of a base fluid blend of a mixture of bis(phenoxyphenoxy)benzenes and trimethylolpropane trienanthate, wherein said mixture of bis(phenoxyphenoxy)benzenes provides from 25 to 75 percent of the total, from about 0.01% to 10% by weight of said base fluid blend, of a 1,3-propanedionato cobalt compound, and from about 0.01% to 10%, by weight of said base fluid blend, of an aromatic amine containing at least two benzene nuclei, the combined amounts of said 1,3-propanedionato cobalt compound and said aromatic amine being sufficient to increase the oxidative stability of said base stock blend.

10. The composition of claim 9 in which said amine is a polyaryl amine.

11. The composition of claim 9, in which said 1,3-propanedionato cobalt compound is bis(2,4-pentanedionato)-cobalt, and said aromatic amine is N-[(1-aminocyclohexyl)methyl]-N′-phenyl-p-phenylenediamine.

12. The composition of claim 9 in which said amine is a poly-N-arylidene amine.

13. A functional fluid composition having a pour point below about 0° F., consisting essentially of a base fluid blend of a mixture of bis(phenoxyphenoxy)benzenes and trimethylolpropane trienanthate, wherein said mixture of bis(phenoxyphenoxy)benzenes provides from 25 to 75 percent of the weight of the total, from about 0.01% to 10%, by weight of said base fluid blend, of N,N′-bis(2-hydroxybenzylidene) - p - phenylene - diamine, and from 0.01% to 10%, by weight of said base fluid blend, of a (2,4-pentanedionato)cobalt compound.

14. The composition of claim **13** in which said cobalt compound is bis(2,4-pentanedionato) cobalt (II).

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