United States Patent Office

3,360,467

Patented Dec. 26, 1967

3,360,467

FUNCTIONAL FLUID

Kenneth L. McHugh, Kirkwood, Mo., and John O. Smith and John R. Stemniski, Swampscott, Mass., assignors to Monsanto Research Corporation, St. Louis, Mo., a corporation of Delaware

No Drawing. Filed Mar. 29, 1965, Ser. No. 443,665
10 Claims. (Cl. 252—74)

This application is a continuation-in-part of our application Ser. No. 182,965, filed Mar. 27, 1962, and now abandoned.

This invention relates to liquid fluids of high thermal stability and more particularly provides functional fluids, e.g., lubricants, comprising polyphenyl ethers and certain metal chelates as adjuvants therefor.

The polyphenyl ethers are of great interest for use as lubricant base stocks because they are thermally stable to 800° F. and thus meet the requirement for high temperature stability which is demanded by new type of aircraft. However, they do not possess outstanding lubricity properties, particularly with respect to resistance to wear and to extreme pressures at high temperatures. Also, although the fact that they are oxidatively stable to about 500° F. makes them superior to other presently available lubricants insofar as oxidative stability is concerned, further improvement in this area is desirable. The matter of oxidative stability is also important when the polyphenyl ethers are employed as other functional fluids, e.g., as heat-exchange media, hydraulic fluids, atomic reactor coolants, diffusion pump fluids, etc. However, for use as high-temperature lubricants, both lubricity and stability to oxidation could stand improvement. This is because, with recent changes in the design of aircraft engines, there is a demand for lubricants which will perform satisfactorily under conditions far more rigorous than even contemplated in the past.

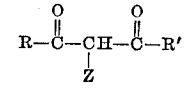
As is known in the art, petroleum lubricants generally comprise, in addition to the petroleum base stock, additives or adjuvants which impart specifically desired properties to the base stock, e.g., rust-inhibitors, anti-oxidants, extreme pressure-resisting agents, lubricity improvers, detersives, etc. The additives proposed heretofore have been designed to accommodate the requirements of petroleum base stocks for lubrication in conventional equipment such as internal combustion engines of the automotive type, diesel engines and the like. One feature in common with respect to these various applications was that the temperature of use was not excessive, i.e., it may vary from about 40° F. to 300° F. With the advent of extremely high speed aircraft of the jet type, it was found that neither the petroleum base stock nor the conventional additives used therewith were practical, because the lubricant and the additives had to be effective at temperatures which were above the decomposition points of the known additives, e.g., at temperatures which were generally within the range of 400° F. to 700° F. It was also found that when conventional additives were employed with lubricants and other functional fluids having higher thermal stability than that possessed by petroleum base stocks, the additives did not perform in a predictable manner, i.e., a material possessing an extreme pressure-resisting effect or an antioxidant effect with the petroleum hydrocarbon

lubricants generally did not possess such effects when used with the polyphenyl ether fluids.

Since the polyphenyl ether fluids are not exceptional in their ability to lubricate metals, lubricity additives are generally required to prevent excessive wear of moving metal parts. Such an additive must not only be stable at the high temperatures to which the polyphenyl ether lubricant is exposed during use, but it must also be noncorrosive to the metal under such conditions. Also, it should not catalyze decomposition and/or oxidation of the polyphenyl ethers at the high temperatures. If an extraneous antioxidant or corrosion-inhibiting agent is present, the anti-wear additive must be non-reactive toward it. Hopefully, the anti-wear additive should also be an antioxidant for the polyphenyl ethers. Inhibiting oxidation of the polyphenyl ethers at the high temperatures is necessary in order to avoid an increase in viscosity of the fluid to the point where it can clog up the mechanism. Since the ethers with which the present invention is concerned are entirely aromatic, oxidation proceeds in a manner which differs essentially from that of compounds having aliphatic carbon. The mechanism whereby the polyphenyl ethers are oxidized at high temperatures is unique compared to the classical mechanisms depicted for the low temperature autooxidations of, e.g., the petroleum hydrocarbons. In the case of the polyphenyl ethers, the initiation step is an attack by molecular oxygen at the phenyl-oxygen-phenyl carbons rather than at the C-H positions as in the case of the paraffinic hydrocarbons. Thereby, there is formed a phenoxy free radical which adds to a polyphenyl ether molecule to form higher molecular weight, fused-ring polyphenyl ethers. Deterioration of the polyphenyl ether is thus demonstrated not by carbonization, but by greatly increased viscosity owing to presence of the very high molecular weight ethers. However, in arriving at a satisfactory lubricity and antioxidant additive for the polyphenyl ethers, the possibility of sludging cannot be over-looked, since use of some additives at the high operating temperatures will result in sludging, even though antioxidant effect is evidenced by lack of viscosity increase in the polyphenyl ether fluid. On the other hand, additives whose use does not bring about the formation of sludge may be found to be ineffective insofar as preventing viscosity increase is concerned.

Accordingly, an object of the present invention is the provision of improved polyphenyl ether fluid compositions. Another object of the invention is the provision of polyphenyl ether lubricants having improving resistance to wear. Still another object is the provision of polyphenyl ether compositions which possess an improved resistance to oxidation. A most important object is provision of polyphenyl ether fluids which are substantially nonsludging.

These and other objects hereinafter disclosed are provided by the invention wherein there is employed as additives for the polyphenyl ether liquid fluids a chelate of a heavy metal of Groups I–IV and VI–VIII of the Periodic Arrangement of Elements and a carbonyl compound of the formula



in which R and R' are selected from the class consisting of alkyl radicals from 1 to 6 carbon atoms and aryl, alkaryl and aralkyl radicals of from 6 to 10 carbon atoms, and Z is selected from the class consisting of hydrogen, R, R', and carboalkoxy radicals of from 2 to 6 carbon atoms.

It will be evident from the above formula that the invention encompasses as additives having one or more effects on the polyphenyl ethers certain metal chelates of aliphatic β-diketones. The metal constituent of the chelate may be, for example, copper, silver or gold of Group I of the Periodic Arrangement of Elements, zinc, cadmium and mercury of Group II, aluminum, gallium, indium and thallium of Group III, titanium, germanium, zirconium, tine and lead of Group IV, manganese and rhenium of Group VII, and iron, cobalt, nickel, ruthenium, palladium, iridium and platinum of Group VIII.

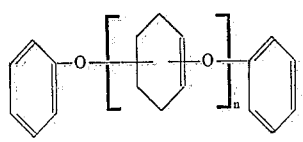
The carbonyl compound may be an aliphatic or aliphatic-aromatic hydrocarbon β-diketone, e.g., acetylacetone, 1,5-diphenyl-2,4-pentanedione, tridecane-4,6-dione, 1-*p*-tolyl-3,5-octanedione, 3-benzyl-2,4-pentanedione or 1,7-di-β-naphthyl-3,5-heptanedione. The carbonyl compound may or may not carry a carboalkoxy group at the carbon atom which is between the two carbonyl groups, e.g., it may be 3-carbomethoxy-2,4-pentanedione, 4-carbopentyloxy-1-phenyl-3,5-hexanedione, or 3-carbobutoxy-1,6-di-α-naphthyl-2,4-pentanedione.

Owing to their easy availability, a very useful class of chelates is that obtained from acetylacetone. For convenience, these will be hereinafter referred to as metal acetylacetonates. They are readily available in known manner by reaction of acetylacetone with a salt of the appropriate metal, e.g., the acetate, chloride or sulfate. Examples of presently useful metal acetylacetonates include the copper, zinc, cadmium, aluminum, zirconium, ferrous, ferric, cobalt, manganous, nickel and indium acetylacetonates.

Other metal chelates of paraffinic β-diketones which can be used as antioxidants for the polyphenyl ethers include:

Manganous chelate of 2,4-hexanedione,
Cadmium chelate of 3-methyl-2,4-pentanedione,
Aluminum chelate of 3,5-heptanedione,
Zirconium chelate of 3,5-octanedione,
Titanium chelate of 2,4-decanedione,
Tin chelate of 7,9-pentadecanedione,
Ferrous chelate of 3-butyl-2,4-pentanedione,
Iridium chelate of 3-hexyl-4,6-nonanedione,
Germanium chelate of 3,5-heptanedione.

The polyphenyl ethers to which this invention pertains can be represented by the structure



where *n* is a whole number from 2 to 5. The preferred polyphenyl ethers are those having all their ether linkages in the meta position since the all-meta linked ethers are the best suited for many applications because of their wide range and high degree of thermal stability. However, mixtures of the polyphenyl ethers, i.e., either isomeric mixtures or mixtures of homologous ethers, can also be used to obtain certain properties, e.g., lower solidification points. Examples of the polyphenyl ethers contemplated are the bis(phenoxyphenyl) ethers, e.g., bis(m-phenoxyphenyl) ether, the bis(phenoxyphenoxy)-benzenes, e.g., m-bis(m-phenoxyphenoxy)benzene, m-bis(p - phenoxyphenoxy)benzene, o - bis(o - phenoxyphenoxy)benzene, the bis(phenoxy - phenoxyphenyl) ethers, e.g., bis[m-(m-phenoxyphenoxy)phenyl] ether, bis[p-(p-phenoxyphenoxy)phenyl] ether, m-[(m-phenoxyphenoxy)phenyl] o-[(o-phenoxyphenoxy)phenyl] ether and the bis(phenoxyphenoxyphenoxy)- benzenes, e.g., m-bis[m-(m-phenoxyphenoxy)phenoxy]benzene, p-bis[p-(m-phenoxyphenoxy)phenoxy]benzene, or m-bis[m-(p-phenoxyphenyl)phenoxy]benzene. It is also contemplated that mixtures of the polyphenyl ethers can be used. For example, mixtures of polyphenyl ethers in which the non-terminal phenylene rings (i.e., those rings enclosed in the brackets in the above structural representation of the polyphenyl ethers contemplated) are linked through oxygen atoms in the meta and para positions, have been found to be particularly suitable as lubricants because such mixtures possess low solidification points and thus provide compositions having wider liquid ranges. Of the mixtures having only meta and para linkages, a preferred polyphenyl ether mixture of this invention is the mixture of 5-ring polyphenyl ethers where 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 about −10° F., whereas the three components solidify individually at temperatures above normal room temperature.

The aforesaid polyphenyl ethers can be obtained by the Ullmann ether synthesis which broadly relates to ether forming reactions, e.g., alkali metal phenoxides such as sodium and potassium phenoxides 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 metal chelates are combined with the fluid polyphenyl ethers to the extent of 0.01% to 1.0% by weight, depending upon the nature of the individual chelate and of the ether fluid. Within these limits, the concentration of chelate at which the desired effects are obtained will vary, depending upon the nature of the chelate and of the polyphenyl ether. It may be readily determined by use of conventional testing procedures known to those skilled in the art. The present chelates possess anti-wear and antioxidant effects on the polyphenyl ethers, generally.

The invention is further illustrated by, but not limited to, the following examples:

EXAMPLE 1

Manganous and lead acetylacetonates were compared with some commonly employed lubricant additives for anti-wear effect when incorporated into a mixture of polyphenyl ethers consisting by weight of:

	Percent
m-Bis(m-phenoxyphenoxy)benzene	65
m-[(m-Phenoxyphenoxy)(p-phenoxyphenoxy)] benzene	30
m-Bis(p-phenoxyphenoxy)benzene	5

Testing was conducted by means of the "Shell 4-Ball Wear Machine." It consists of an equilateral tetrahedron formed by 4 stainless steel balls with the three lower balls immovably clamped in a ball holder. In the present tests, the upper ball was rotated about the vertical axis in contact with the 3 lower stationary balls under a 40 kg. load for one hour at 400° F. The contacting surfaces were immersed in the test fluid and the circular scars worn in the surface of the three stationary balls were measured by means of a low power microscope. A modified cup and heater assembly was used to evaluate lubricants at the 400° F. temperature; see "The Study of Lubrication Using the Four-Ball Type Machine," R. G. Larsen, Lublication Engineering, 1, pages 35–43, 59, August 1945.

Employing the above procedure, the results shown in

Table I were obtained with the additives shown therein at the indicated concentrations:

TABLE I

Additive	Concn., weight percent	Scar diameter, mm.
None		3.30
Manganous acetylacetonate	0.5	1.19
Lead acetylacetonate	0.5	1.18
Bis(triphenylphosphine)nickel dibromide	0.5	3.45
Diphenylmercury	1.0	3.32
Tropylidene molybdenum tricarbonyl	0.5	3.31
Boron trifluoride/Ni dimethylglyoxime complex	1.0	3.38
Bis(triphenylphosphine)nickel dithiocyanate	0.5	3.39
2,4,6-triphenylphenol	1.0	3.36
N-nitroso-N-phenylbenzylamine	1.0	3.04
2,2'-dipyridylamine	1.0	3.53

EXAMPLE 2

The mixture of polyphenyl ethers described in Example 1 were incorporated with ferric or with manganous acetylacetonate and then submitted to the Falex test for the purpose of determining extreme-pressure resisting properties. This test is described in the articles by V. A. Ryan in "Lubrication Engineering," September 1946, and by S. Kyropoulos in "Refiner Natural Gasoline Mfr.," 18, 320–24 (1939). Briefly, the test was conducted as follows:

There was employed a Faville-LeVally Falex lubricant testing machine with heating element, 4,500 lb. pressure gage indicating bearing loads, calibrated, circular, toothed loader capable of providing wear estimates, and torque indicating gage. The machine is essentially a device in which a pin is rotated between two V-shaped bearing blocks which are immersed in an oil cup containing 55 ml. of the lubricant which is to be tested. The bearing blocks are inserted in self-aligning recesses in the short lever arms, or jaws, of the loading-applying mechanism. Pressure is applied through the loading mechanism which fits loosely over the bifurcated ends of the long level arms. The ratchet wheel is turned up by hand until the loading mechanism takes hold, which is indicated by registration of applied load on its attached gage. Additional load is applied by engaging the load-applying arm with the ratchet wheel. The eccentric motion of the load-applying arm increases the application of load, one tooth at a time. The entire mechanism is free to swing about its axis, this tendency to turn being resisted by the syphon operated gage which registers torque in pound-inches. In the present tests, the machine was operated at 290 r.p.m.

Employing the above-described procedure, the Falex reading for said mixture of polyphenyl ethers containing a 1.0% by weight concentration of ferric acetylacetonate was 1750 and that for said mixture of polyphenyl ethers containing an 0.5% concentration of manganous acetylacetonate was 2250. That for the same mixture of polyphenyl ethers in absence of any additive was 500.

EXAMPLE 3

A number of metal acetylacetonates were compared with some commonly employed lubricant additives for inhibition of viscosity increase at high temperature in the presence of oxygen. The base stock was the mixture of polyphenyl ethers described in Example 1. Testing was conducted as follows:

Samples were prepared consisting of 20 ml. of said mixture of ethers and the concentration of additive shown below. The sample was heated to 100° F., and the viscosity of the sample was determined at this temperature. The temperature was then increased to 600° F., and while holding the sample at this temperature, air was bubbled through it at a rate of 1 liter per hour, for either 24 or 48 hours as shown below. The sample was then allowed to cool, the viscosity was re-determined at 100° F., and the percent increase in viscosity was calculated. The results shown in Table II were obtained.

TABLE II

Additive	Concn. percent weight	Time, hours	Viscosity Increase, percent
Co acetylacetonate	0.5	24	10.9
Mn^{II} acetylacetonate	0.5	24	10.1
Ni acetylacetonate	0.5	24	12.9
Fe^{II} acetylacetonate	0.5	24	16.8
Ti acetylacetonate	0.5	24	19.9
Al acetylacetonate	1.0	24	20.7
In acetylacetonate	0.5	48	20.2
Cu chelate of 2-phenyl-2-mercaptoethylphenyl ketone	1.0	48	45.9
Tin titanium malonate	0.5	48	40.2
Bis(N,N-dimethylamino)titanium dichloride	0.5	48	90.6
Diphenyltin bis(didecyldithiophosphate)	1.0	48	123.0
Reaction product of hydroquinone and dibutyltin oxide	0.5	48	56.2
Tropylidene molybdenum tricarbonyl	0.5	24	173.0
Bis(p-phenoxyphenyl)mercury	1.0	24	48.2
Ni bis(N-phenyl-5-nitrosalicylimine) and trichloroacetic acid (2:1)	3.0	24	64
Diphenylamine	1.0	24	73.3
2,4,6-triphenylphenol	1.0	24	59.0
Phenylbiphenylamine	1.0	48	116.9
Triphenylphosphine/triphenylboron complex	1.0	24	67.7
Tetraphenylsilane	1.0	24	52.1
Tetraphenylgermane	0.5	24	53.0
Triphenylarsine	1.0	24	50.0

EXAMPLE 4

The effect of the presence of some metals on inhibition of viscosity increase by various additives, including various acetylacetonates, is described in this example.

Respective samples of the mixtures of ethers of Example 1 were incorporated with the concentration of additive noted below and the same quantity in each case of pieces of copper, aluminum and steel wire. Air was passed through the samples at the rate of 1 liter per hour for the time shown below while maintaining the samples at 600° F., and the increase in viscosity thereby produced was determined at 100° F. The results shown in Table III were thereby obtained:

TABLE III

Additive	Concn. percent weight	Time, hours	Viscosity Increase, percent
Co acetylacetonate	0.5	24	4.9
Cu acetylacetonate	0.5	24	10.0
Ferrous acetylacetonate	0.5	24	15.2
Mn^{II} acetylacetonate	0.5	24	15.4
Aluminum acetylacetonate	1.0	24	13.2
Ti acetylacetonate	0.5	24	13.0
Nickel acetylacetonate	1.0	24	24.3
Ferric acetylacetonate	1.0	24	24.5
In acetylacetonate	0.5	48	12.1
Bis(tributylphosphine)nickel chloride	1.0	24	83.0
Tripyridylmolybdenum tricarbonyl	0.5	24	107.2
Triphenylphosphinemolybdenum pentacarbonyl	0.5	24	134.1
o-Biphenyl silicate	1.0	24	150.5
Ni chelate of 2-phenyl-2-mercaptoethyl. phenyl ketone	1.0	48	156.0
Ni bis(N-p-phenoxyphenoxyphenyl-5-nitrosalicylimine)	2.0	24	122.0
o-tert-Butylaniline	1.0	24	113.9
2,6 di-tert-butyl-4-methylaniline	1.0	24	204.7
p-Tolyl sulfoxide	1.0	24	111.4

EXAMPLE 5

In this example there are shown the simultaneous anticorrosive and viscosity-increase inhibiting effects of cobalt acetylacetonate and of titanium acetylacetonate as compared to other additives. Testing was conducted as follows:

Respective samples of the mixture of ethers described in Example 1 were incorporated with the concentration of additive shown below in Table IV and with the same quantity in each sample of metallic copper, steel, aluminum, silver and titanium. The viscosity of each sample was determined at 100° F. Air was then passed through each sample at the rate of 1 liter/hour for 24 hours while

maintaining the test sample at 600° F. The increase in viscosity thereby produced was determined at 100° F., and the change in weight for the copper, steel, aluminum, silver and titanium was determined. The results thus obtained are shown in Table IV.

TABLE IV

Additive	Viscosity Increase, Percent	Cu	Steel	Al	Ag	Ti
Co acetylacetonate, 0.5%	4.4	0.32	0.32	0.12	0.12	0.00
Ti acetylacetonate, 0.5%	8.8	0.24	0.04	−0.20	0.04	0.95
Bis(triphenylphosphine) iron tricarbonyl, 0.5%	13.60	−14.20	2.60	−26.00	12.70	1.50
Thiobisphenol, 0.5%	48.80	−0.08	0.12	0.08	0.08	1.60

EXAMPLE 6

In this example there are shown the simultaneous viscosity-increase inhibiting and anti-sludging effects of cobalt acetylacetonate and ferric acetylacetonate as compared to other additives. Testing was conducted according to the procedure of specification MIL–L–9236A (Federal Specification 791 Method 5308.2), which test determines stability to oxidation in the presence of metals by determining viscosity change and the formation of sludge; however, the tests were conducted at 650° F. instead of at 500° F., as called for by said specification. In each test, the base stock was the mixture of polyphenyl ethers described in Example 1, and in each test the additive was present in a 0.5% concentration. The tests were run for a period of 48 hours.

The results obtained are set forth in Table V. With respect to the data in the column of the table headed "Viscosity Increase, percent" such data were obtained by measuring the viscosity, at 100° F., of the polyphenyl ether mixture plus additive before and after completion of the oxidation tests and reporting the differences as a percent increase based on the original viscosity. In the case of the column identified "Deposit Rating," the numbers therein are ratings based on a scale from 1 to 4, with 1 being essentially none and 4 heavy deposit of sludge.

TABLE V

Additive	Viscosity Increase, Percent	Deposit Rating
Cobalt acetylacetonate	18.6	1
Ferric acetylacetonate	39.3	1
Triphenylbismuthine	86.9	4
Cyclooctatetraene iron carbonyl	94.2	2
Tetraphenylgermanium	102.5	1
Bismuth o-chlorobenzoate	114.4	1
Nickelocene	117	3
Bis(p-phenoxyphenyl)mercury	500	1
Di-o-biphenylylmercury	500	1
None (control)	500	2

The data of Table V show that while many materials serve to suppress sludging of the polyphenyl ethers under severe temperature and oxidation conditions, the metal chelates are unique in that they function simultaneously as very good viscosity-increase inhibitors and as inhibitors of sludge deposits.

The present metal chelates contribute anti-wear pressure-resisting, sludge-inhibiting, corrosion-resisting and antioxidant properties to the polyphenyl ether fluids, generally. Thus, instead of the mixture of 65% by weight of m-bis(m-phenoxyphenoxy)benzene, 30% by weight of m-[m-phenoxyphenoxy)(p - phenoxyphenoxy)]benzene and 5% m-bis(p-phenoxyphenoxy)benzene which was used in the above examples, the polyphenyl ether component may be any one polyphenyl ether having from 4 to 7 benzene rings. For example, manganous or nickel acetylacetonate can be a very good anti-wear additive for any one of the three ethers of the polyphenyl ether mixture of the above examples, as well as for such other polyphenyl ethers as p-bis[p-(m-phenoxyphenoxy)phenoxy]benzene or m-[(m-phenoxyphenoxy)(o-phenoxyphenoxy)]benzene, or m-bis[m-(p-phenoxyphenoxy)phenoxy]benzene, or mixtures thereof in any proportion. Lubricant mixtures of ethers are generally so constituted as to give simultaneously an optimum of thermal stability and lubricity at the temperatures to which they will be exposed in operation; but since the polyphenyl ethers, generally, are benefited by the metal chelates with respect to increasing stability to wear and to oxygen at high temperatures, mixtures having varying proportions of the ethers are advantageously modified by the present additives.

Although the present metal chelates, generally, confer a plurality of adjuvant effects including lubricity and antioxidant properties to the polyphenyl ether fluids, a single metal chelate does not necessarily impart all of these properties to the polyphenyl ethers simultaneously. One metal chelate may be more effective than another with respect to conferring a desired property; and within the 0.01% to 1.0% concentration range, a greater amount of a certain chelate may be required to impart one property, e.g., antiwear effect, than is required to impart another property, e.g., antisludging effect. Therefore, although a plurality of the adjuvant effects are generally demonstrated by a single metal chelate, two or more chelates may be used together advantageously: one to provide a certain effect at the lowest possible concentration and another one to provide a diverse effect, also at the lowest possible concentration. Selection of the proper metal chelate and the optimum concentration thereof for obtaining the desired benefit is simply a matter of routine testing by one skilled in the art.

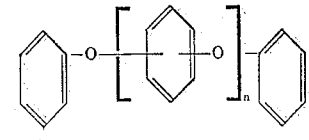
Polyphenyl ether fluids containing the present chelate additives are particularly useful as high temperature lubricants because they possess good antiwear and/or extreme-pressure resisting property while at the same time possessing good resistance to oxygen at very high temperatures. However, compositions consisting of the polyphenyl ethers and the present chelate additives are also advantageously employed in other functional fluid applications, e.g., as hydraulic fluids and as heat-exchange media. The chelate additives inhibit viscosity increase in the presence of oxygen at high temperatures and also prevent sludging and corrosion; hence, these additives render the polyphenyl ethers suitable for use in any application in which is involved exposure to oxygen and/or metal at temperatures of up to, say, the decomposition point of the polyphenyl ethers.

The metal chelates may be used in the polyphenyl ethers with other additives, e.g., pour point depressants, viscosity index improvers, dyes, etc.

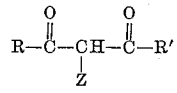
Other modes of applying the principles of this invention may be employed instead of these specifically set forth above, changes being made as regards the details herein disclosed, provided the elements set forth in any of the following claims, or equivalents thereof may be employed.

What we claim is:

1. A liquid fluid composition consisting essentially of a polyphenyl ether of the formula



wherein n is a whole number of from 2 to 5 and from 0.01% to 1.0%, by weight of the ether, of a chelate of a heavy metal of Groups I–IV and VII–VIII of the periodic Arrangement of Elements and a carbonyl compound of the formula



wherein R and R′ are selected from the class consisting of alkyl radicals of from 1 to 6 carbon atoms and aryl, alkaryl and aralkyl radicals of from 6 to 10 carbon atoms and Z is selected from the class consisting of hydrogen, R, and R′, and carboalkoxy radicals of from 2 to 6 carbon atoms.

2. The composition defined in claim **1**, further limited in that Z is hydrogen.

3. The composition defined in claim **1**, further limited in that the carbonyl compound is acetylacetone.

4. The composition defined in claim **1**, further limited in that the chelate is cobalt acetylacetonate.

5. The composition defined in claim **1**, further limited in that the chelate is manganous acetylacetonate.

6. The composition defined in claim **1**, further limited in that the chelate is ferric acetylacetonate.

7. The composition defined in claim **1**, further limited in that the chelate is indium acetylacetonate.

8. The composition defined in claim **1**, further limited in that the chelate is lead acetylacetonate.

9. The composition defined in claim **1**, further limited in that the chelate is the ferrous acetylacetonate.

10. The composition defined in claim **1**, further limited in that the chelate is the nickel acetylacetonate.

References Cited

UNITED STATES PATENTS

2,460,700	2/1949	Lyons	252—74 X
2,795,549	6/1957	Abbott et al.	252—74 X
3,006,852	10/1956	Barnum et al.	252—52

FOREIGN PATENTS

851,651	10/1960	Great Britain.

LEON D. ROSDOL, *Primary Examiner.*

S. D. SCHWARTZ, R. D. LOVERING,
Assistant Examiners.