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HIGH-TEMPERATURE LUBRICANTS

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This invention relates to lubricating compositions. More particularly, it relates to lubricating compositions especially designed for use at elevated temperatures and under oxidizing conditions.

Aircraft and gas-turbine engine lubricants require special properties, such as high-temperature stability, and oxidation stability which are not possessed to a sufficient degree by conventional lubricants. They must possess a high viscosity index in order to provide adequate lubrication over a wide range of temperatures. They must be thermally stable and must be either stable to oxidation or amenable to stabilization against oxidation in order that they may retain their usual properties after operation for extended periods at high temperatures. While it is preferred that they have low pour points, this is not essential, since the mechanisms containing them may be heated in such a way as to maintain high-pour-point materials in a fluid condition during down time or cold operating periods.

Many fluids have been proposed for operation under such conditions but for the most part each of them inherently possesses one or more shortcomings making their use undesirable in that respect. For example, the silicone fluids are extremely stable at high temperatures but are notorious for their poor lubricating properties. Ester lubricants on the other hand are excellent where low operating temperatures are concerned due to their low pour points and high viscosity indices, but for the most part do not have satisfactory thermal stability at temperatures in the order of 400° F. and above.

Mineral lubricating oils which exhibit satisfactory low-temperature viscosities have generally been found to have flash points that are dangerously low and high-temperature viscosities that are below those required. In other words, when the mineral oil is thin enough at low temperatures, it is too volatile at high temperatures, where it is also too thin to possess satisfactory lubricity. It has been found that generally speaking additive agents do not enhance these essential properties to a satisfactory extent.

One of the most important properties that any lubricant must possess in addition to those normally associated with lubricants, such as a suitable viscosity and sufficient lubricity, is that of a combination of high thermal stability and oxidation stability. The latter property constitutes a basic and essential attribute which can be satisfied in one of two ways and preferably a combination of both. This constitutes an inherent stability against degradation due to oxidation or the ability of the compound to respond to stabilization against oxidation by the presence of additive materials. Under ordinary temperature conditions, such as those existing in ordinary lubrication up to about 400° F., the stabilization of organic materials is not regarded as being especially difficult since many compounds are known and available which will stabilize such materials under these relatively low-temperature conditions. However, as temperatures are raised, such as in the operation of aircraft and gas-turbine engines, there is a drastic change in the course of oxidation

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and the ability of known compounds to prevent the oxidation of organic materials. Up to the present time where operation of organic fluids over for about 400° F., was concerned, it has been necessary in most instances to depend upon the inherent oxidation stability of the fluid per se since virtually no additive materials were known which would stabilize a substance at these elevated temperatures. The rate of oxidation accelerates rapidly as the temperatures are raised and many compounds which normally perform a function of oxidation stabilization at lower temperatures reverse their roles at elevated temperatures and indeed become pro-oxidant substances.

Recent studies in the synthetic lubricant fields have indicated that certain restricted classes of polyphenyl ethers have excellent thermal stability and possess sufficient oxidation resistance as an inherent characteristic for use at extremely high operating temperatures. Unfortunately, however, even these stable materials are of limited utility especially when the temperatures exceed about 450° F. since they tend to decompose and must be either replenished or replaced within relatively short periods.

It is an object of the present invention to provide improved lubricant compositions especially useful for operation of engines, motors and moving metallic elements at high operating temperatures. It is a particular object of this invention to extend the operating life of certain polyphenyl ethers at operating temperatures exceeding about 450° F. in the presence of oxidizing conditions. Other objects will become apparent during the following detailed description of the invention.

Now, in accordance with the present invention, compositions are provided which are especially useful for lubricating purposes at elevated temperatures comprising a major proportion of polyphenyl ethers and minor proportions sufficient to stabilize said ethers against oxidation at temperatures in excess of about 450° F., said additive material being basic and neutral indium salts of fatty acids, thiafatty acids, and of alkylated benzoic acids, all as more particularly defined hereinafter. Still in accordance with the present invention, especially useful results have been obtained even when catalytic amounts of copper are present by the synergistic combination of one of at least one of the above-named indium salts with additive proportions of a bromo-phenyl ether and of a bis-alkylated phenol monosulfide.

As stated hereinbefore, the stabilization against oxidation of organic substances at temperatures in excess of about 450° F. is extremely difficult and may follow a different mechanism than that which occurs at lower operating temperatures.

The indium salts found to be effective for the present purpose include the neutral or basic salts of fatty acids, especially those having from 8 to 15 carbon atoms per molecule; indium salts of alkyl mercapto fatty acids, otherwise known as thiafatty acids; and indium salts of alkylated benzoic acids, the latter being indium salts of benzoic acid derivatives wherein the benzoic acid nucleus bears 1-4 alkyl radicals having 3-10 carbon atoms each. Table I which follows lists typical indium salts coming within the limits defined above. It will be noted that the fatty acids include not only the straight-chain fatty acids but also branched-chain fatty acids. Also, the thiafatty acids may be those in which the mercapto radical is attached to a secondary carbon atom or to a tertiary carbon atom. In effect, this differentiates between straight-chain thiafatty acids and branched-chain thiafatty acids. It is preferred that the mercapto radical contain an aliphatic hydrocarbon radical having from 4-12 carbon atoms each and that the hydrocarbon radical separating the carboxyl group be an aliphatic radical having from 1-4 carbon atoms each.

While the indium salts are highly effective for stabilizing polyphenyl ethers as defined hereinafter against oxidation at temperatures above about 400° F., it has been found that this stabilizing activity is markedly reduced if catalysts, such as copper, are present. However, in accordance with the present invention the effect of copper catalyst is minimized to a substantial extent if the indium salt is combined with a bromophenyl ether and a diphenyl monosulfide. The bromophenyl ethers are preferably unsubstituted with radicals directly attached to the phenyl group other than bromine, but may bear either tertiary-butyl or alphacumyl radicals without adverse effects.

TABLE I

Indium salts

A. Salts of fatty acids:

Straight-chain—

- n-Octanoic acid
- n-Decanoic acid
- n-Tridecanoic acid
- n-Pentadecanoic acid

Branched-chain—

- 2-ethyl hexoic acid
- 2-ethyl decanoic acid
- 2-ethyl tridecanoic acid
- 3-n-butyl hexanoic acid
- 3-tert-butyl hexanoic acid
- 2,4-dimethylhexanoic acid
- 2,4-dimethyl-3-ethyl hexanoic acid

B. Salts of alkyl mercapto fatty acids:

- 3-thiatridecanoic acid
- 4-thiadodecanoic acid
- 5-thiaheptadecanoic acid
- 3-thiatetradecanoic acid
- 4-thiatridecanoic acid
- 5-thiapentadecanoic acid

C. Salts of alkylated benzoic acids:

- p-(n-Octyl) benzoic acid
- p-(2-ethylhexyl) benzoic acid
- m-(n-Hexyl) benzoic acid
- m-(3-methyloctyl) benzoic acid
- 2,3-dimethyl-4-(n-octyl) benzoic acid
- 2,4-di(n-heptyl) benzoic acid

According to Table II, it will be seen that the bromophenyl ethers useful in conjunction with the other two types of additives include the mono- and di-bromo-phenyl materials in which the bromine radicals may be ortho, meta or para with respect to the position of the ether linkage. Moreover, the ethers may be mixed ethers wherein the two bromo-phenyl radicals differ either with respect to the position of the bromine atom, with respect to the number of bromine radicals attached to the phenyl radical or with respect to the presence or absence of tertiary-butyl or alpha-cumyl radicals. The bromo-phenyl ethers may be deliberately added to the polyphenyl ethers but may occur as an unconsumed reactant since one method of forming the polyphenyl ethers is by use of the bromo-phenyl ethers. It will be understood that the unsubstituted bromo-phenyl ethers listed in Table II may be modified by the presence of tertiary butyl or alpha cumyl radicals on one or both of the bromo-phenyl radicals. The unsubstituted bromo-phenyl ethers and particularly the unsubstituted bis(monobromophenyl)ethers are preferred.

TABLE II

Bromo phenyl ethers

- Bis(p-bromophenyl) ether
- Bis(m-bromophenyl) ether
- Bis(o-bromophenyl) ether
- (p-Bromophenyl) (m-bromophenyl) ether
- (p-Bromophenyl) (o-bromophenyl) ether
- (m-Bromophenyl) (o-bromophenyl) ether
- Bis(2,4-dibromophenyl) ether

- Bis(2,3-dibromophenyl) ether
- Bis(2,5-dibromophenyl) ether

As the data given hereinafter will show, the presence of a combination of bromophenyl ether with an indium salt does not provide the full protection required in the present composition. This must be supplemented particularly in the presence of a copper catalyst by a third additive, namely, a diphenol monosulfide. Typical species of these materials are given in Table III which follows:

TABLE III

Diphenol monosulfides

- Di(4-hydroxyphenyl) monosulfide
- Di(2-hydroxy-5-phenylphenyl) monosulfide
- Di(2-hydroxy-5-t-amylphenyl) monosulfide
- Di(3,5-dimethyl-4-hydroxyphenyl) monosulfide
- Di(3-methyl-4-hydroxy-5-butylphenyl) monosulfide
- Di(3-amyl-4-hydroxyphenyl) monosulfide
- Di(2-methyl-4-hydroxy-5-butylphenyl) monosulfide
- Di(2-methyl-4-hydroxy-5-propylphenyl) monosulfide
- Di(3-phenyl-4-hydroxyphenyl) monosulfide
- Di(2-methyl-4-hydroxy-5-cyclohexylphenyl) monosulfide
- Di(2-hydroxy-3-butyl-6-methylphenyl) monosulfide
- Di(2-hydroxy-3-butyl-5-methylphenyl) monosulfide
- Di(2-hydroxy-3-t-butyl-5-methylphenyl) monosulfide
- Di(2-hydroxy-3-methyl-5-phenylphenyl) monosulfide
- Di(2-hydroxy-3,5-di-sec-amylphenyl) monosulfide
- Di(2-hydroxy-3-butyl-5,6-dimethylphenyl) monosulfide
- Di(2-hydroxy-3-cyclohexyl-5-ethylphenyl) monosulfide

The preferred category of the diphenol monosulfides includes those in which the phenol radical is modified by the presence of tertiary alkyl groups, preferably tertiary butyl groups. The monosulfide phenol radical may be modified by the presence of 1-4 alkyl radicals (including cycloalkyl radicals) having from 1 to 8 carbon atoms each. The preferred species which has been found to be highly effective in the compositions of this invention is di(2-hydroxy-3-tertiary butyl-5-methylphenyl) monosulfide.

The data which follow show that the monosulfide must be combined with the other two additives described above in order to provide a polyphenyl ether composition which is stable against oxidation at elevated temperatures. The combination of the monosulfide with either the bromophenyl ether alone or with the indium salt alone does not provide satisfactory stabilization especially in the presence of copper catalysts for the oxidation reaction.

The polyphenyl ethers subject to stabilization against oxidation by means of either the indium salts or the combination of additives described above are confined to the varieties which are unsubstituted polyphenyl ethers or those which are substituted with either tertiary butyl radicals or with alpha-cumyl radicals or both. While the stabilizers are most effective when used with the substituted ethers, they enhance the initially excellent stability of the unsubstituted ethers as well. The presence of other substituents, such as methyl radicals and the like, is undesirable and is not contemplated as falling within the scope of the present invention. This is due to the fact that the presence of these undesired substituents causes the formation of polyphenyl ethers which are not subject to adequate oxidation stabilization when the elevated temperature is contemplated or involved.

The unsubstituted polyphenyl ethers have been found to be outstandingly stable but may be improved in their operating life at temperatures above 400° F. by the presence of the subject classes of additives as described herein. However, the major use of the present invention is with respect to the two other types of polyphenyl ethers, namely, those containing tertiary butyl substituents, alpha-cumyl substituents or both. Mixtures of the unsubstituted polyphenyl ethers with the tertiary butyl or alpha-cumyl substituted ethers is contemplated.

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It is furthermore contemplated to utilize polyphenyl ethers containing ortho, meta or para linkages and preferably a mixture of these linkages so as to promote relatively low pour points in the materials. The meta linkage has been found to be that which produces polyphenyl ethers having the lowest pour points. Consequently, in accordance with the present invention, compositions are provided which are especially useful for lubricating purposes and have good lubricating oil pour points comprising certain restricted classes of polyphenyl ethers, at least two of said ethers being present in the composition and at least one-third of the linkages between phenyl radicals being in meta positions relative to each other. More particularly, and in order to maintain the maximum thermal stability, the polyphenyl ethers with which this invention is concerned are restricted to the unsubstituted polyphenyl ethers and those containing tertiary-butyl and/or alpha-cumyl substituents as well as ethers in which up two-thirds of the oxygen linkages are replaced with isopropylidene linkages. Still in accordance with this invention it is preferred that the mixture of polyphenyl ethers have an average of 3-8 phenyl radicals per molecule and preferably between 4 and 6 phenyl radicals per molecule.

A preferred form of the present invention comprises a mixture of the subject classes of polyphenyl ethers wherein at least one member of the mixture contains both meta linkages between phenyl groups and ortho or para linkages within the same molecule. This is an especially effective way of reducing the pour point of the mixture in addition to mixing two non-identical polyphenyl ethers. The effect is magnified when the proportion of meta linkages is at least two-thirds of those present and preferably between about 75 and 90% of the linkages, the remaining being either ortho or para linkages, preferably para. When the polyphenyl ether comprises one in which there is an oxygen linkage between two groups of polyphenyl linkages, it is sufficient that at least 50% of the linkages other than the one specified oxygen linkage are in the meta position relative to said ether linkage. As stated hereinbefore, these additional linkages between phenyl radicals may be either oxygen or isopropylidene. Table IV, which follows, lists typical polyphenyl ethers which may comprise principal or minor components in the mixtures under consideration.

TABLE IV

Polyphenyl ethers

Bis(meta-phenoxyphenyl)ether
 Bis(para-phenoxyphenyl)ether
 Bis(ortho-phenoxyphenyl)ether
 Meta-bis(meta-phenoxyphenoxy)benzene
 Meta-bis(para-phenoxyphenoxy)benzene
 Para-bis(meta-phenoxyphenoxy)benzene
 Meta(meta - phenoxyphenoxy)(meta-tert-butylphenoxy-phenoxy)benzene
 Meta(meta-alpha-cumylphenoxyphenoxy)(meta-phenoxy-phenoxy)benzene
 Meta(meta-tert-butylphenoxyphenoxy)(para - tert - butyl-phenoxyphenoxy)benzene

It is preferred that from the above types of polyphenyl ethers at least 50% of the mixture be a species either containing nothing but meta linkages or wherein at least about 60% of the mixture comprising the lubricating composition be a species of polyphenyl ether wherein at least about two-thirds of the linkages between phenyl radicals are in the meta position relative to each other. Furthermore, it is preferred that at least about 25% (e.g. 25-75% by weight) of the composition be unsubstituted polyphenyl ethers containing nothing but oxygen linkages between phenyl radicals and bearing no substituents on the carbocyclic rings other than hydrogen.

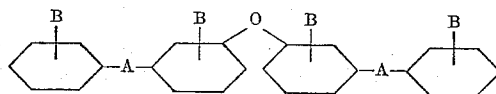
It is within the contemplation of the present invention to provide compositions wherein no unsubstituted poly-

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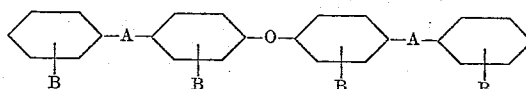
phenyl ethers are present, the compositions being composed of single species or mixtures of tertiary butyl substituted polyphenyl ethers, alpha-cumyl substituted polyphenyl ethers or polyphenyl ethers wherein a substantial portion of the oxygen linkages are replaced with isopropylidene linkages. Still more explicitly, mixtures of the latter types may comprise two or more tertiary butyl substituted polyphenyl ethers, two or more alpha-cumyl substituted ethers or two or more polyphenyl ethers containing isopropylidene linkages substituted for a portion of the oxygen linkages. It is also possible to provide mixtures comprising one or more tertiary butyl substituted polyphenyl ethers with one or more of the other two types of derivative classes.

Mixtures of polyphenyl ethers comprising the preferred base fluid to be used in the present invention include those wherein at least about one-third and preferably 35-60% of the inter-phenyl linkages are in meta relationship to each other and wherein between about 40 and 100% by weight thereof are oxygen linkages, the remaining linkages being either oxygen or isopropylidene. The reaction mixtures are normally liquid at room temperatures although some of the higher average molecular weight mixtures may be low-melting solids. For many purposes, this is not a disadvantage since such materials are especially useful for use where high temperatures are involved. Since the individual components of the lubricant mixtures when unmodified by the isomeric materials as described herewith have pour points substantially above room temperature, it will be seen that the present mixtures have a definite advantage when the intended purpose is that of an operating fluid for engines, motors or radiation-emitting equipment.

In summary, preferred mixtures comprise an ether having the configuration



together with an ether having the configuration



wherein A is a radical of the group consisting of oxygen and isopropylidene and B is a radical of the group consisting of tert-butyl, alpha cumyl and hydrogen, the mol ratio of the first ether to the second ether being between about 1:2 to 9:1.

When utilizing mixtures of unsubstituted polyphenyl ethers with the tertiary butyl or alpha-cumyl substituted polyphenyl ethers, it is preferred that the composition contain from 10 to 90% of unsubstituted ethers containing 2-6 phenyl radicals per molecule together with 90-10% by weight based on the total composition of the substituted polyphenyl ethers as defined above. The principal function of the unsubstituted polyphenyl ethers is to enhance the outstanding high-temperature stability which this class of compounds has been found to exhibit. The substituted polyphenyl ethers as outlined above impart low melting points and in mixture with the unsubstituted polyphenyl ethers causes the melting point of the entire composition to be substantially lower than that of the unsubstituted polyphenyl ethers themselves.

The proportion of additives present in the composition will depend in part upon the temperature and other conditions which the composition will be expected to encounter. Normally, the proportion of additive will be in the order of 0.25-2.5% by weight based on the total composition. This is true when the indium salt is used alone and, in the case of a triple combination of additives, the proportion of each additive will be within the above recited range. Proportions of the additives above

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about 3% have been found to be somewhat less effective than when the additive is present in the order of 0.5–1.5% by weight.

The following data illustrate the use of the present invention; the test given having been performed with bis[para-(para-tertiary-butyl-phenoxy)phenyl]ether. It is to be emphasized, however, that this is merely a typical ether of the group considered and that similar results are obtained when other polyphenyl ethers falling within the scope of the present invention are employed either alone or in conjunction with the material tested. As typical indium salts, indium 2-ethylhexanoate, indium 3-thiatri-decanoate and indium para-octylbenzoate were employed. These were tested in the base stock at temperatures of 500°, 525° and 550° F., the test conditions being essentially those to be found in the Dornite oxidation test equipment as follows: Temperature as above; oxidizing medium; pure oxygen at 760 mm. pressure, recirculated at 25 cc./minute through a 5-gram sample of material under test.

Table V shows that the indium salts substantially increase the life of the material especially under conditions where no adverse catalyst, such as copper or iron, is present:

TABLE V
500° F., Dornite oxygen-absorption test

Additive	0.5 mol O ₂ (per 500 g.), Absorption Time, hr.	Antioxidant Effectiveness Ratio	
		No Catalyst	
None	43		2.1
0.5% Indium 2-ethylhexanoate	89		1.9
1% Indium 3-thiatri-decanoate	83		

Table VI shows that the effect of stabilizers becomes more pronounced at 525° F. and this appears to be optimum of the range of temperatures tested. It will be noted that the three classes of indium salts are roughly equivalent in their stabilizing ability when no catalyst is present. The stabilizers have little effect upon the life of the material when a copper catalyst is present at this temperature, but a substantial effect is noted when the catalyst present is iron. However, at 550° F. (see Table VIII) a beneficial effect is obtained from the use of the indium salts either when no catalyst is present or when either copper or iron catalyst is involved.

TABLE VI
525° F. Dornite oxygen-absorption test

Additive	0.5 mol O ₂ (per 500 g.), Adsorption Time, hr.			Antioxidant Effectiveness Ratio	
	No Catalyst	Cu	Fe	No Catalyst	Fe
None	13.5	5.9	10.8		
0.5% Indium 2-ethylhexanoate	31		25	2.3	2.5
0.5% Indium Caprylate	29	6.6	16	2.1	1.5
1% Indium p-octyl benzoate	33.3			2.5	
1% Indium 3-thiatri-decanoate	30	6.4	23.2	2.2	2.2

Table VII demonstrates the synergistic effect obtained by the combination of the three additives specified, namely, the indium salt, the phenol sulfide, and the bromo-ether. According to Table VII, it will be seen that even in the presence of a copper catalyst the combination of the three additives provides outstanding oxidation stability. The data also show that it is necessary for all three additives to be present, any single one or combination of two of the additives being insufficient for this purpose.

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TABLE VII

Synergistic composition, 525° F. Dornite copper-catalyzed oxygen-absorption test

Additives	0.5 mol O ₂ (per 500 g.), Absorption Time, hr.	Antioxidant Effectiveness Ratio	
None	5.9		
1% Indium Salt ¹	5.9		1.0
1% Phenol Sulfide ²	3.4		0.6
0.5% Bromo Ether ³	5.7		1.0
1% Salt+1% Sulfide	7.8		1.3
1% Salt+0.5% Bromo-ether	12.1		1.7
1% Sulfide+0.5% Bromo-ether	3.1		0.5
1% Salt+1% Sulfide+0.5% Bromo-ether	22.3		3.8

¹ Indium 2-ethylhexanoate.

² Bis (2-hydroxy-3-tert-butyl-5-methylphenyl) sulfide.

³ Bis(p-bromophenyl)ether.

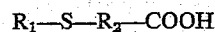
TABLE VIII

550° F. Dornite oxygen absorption test

Additives	0.5 mol O ₂ (per 500 g.), Adsorption Time, hr.			Antioxidant Effectiveness Ratio		
	No Catalyst	Cu	Fe	No Catalyst	Cu	Fe
None	4.5	2.4	4.1			
0.5% Indium 2-ethylhexanoate	5.9			1.3		
0.5% Indium caprylate	7.5			1.7		
1% Indium 3-thiatri-decanoate	10.5	3.4	7.8	2.3	1.4	1.9

I claim as my invention:

1. As a new lubricating composition a major proportion of bis[p-(p-tert-butylphenoxyphenyl)]ether and 0.25–2.5% by weight each of bis (p-bromophenyl) ether, bis (2-hydroxy-3-tert-butyl-5-methylphenyl) sulfide and indium caprylate.
2. As a new lubricating composition a major proportion of polyphenyl ethers having 3–8 phenyl radicals per molecule, at least one-third of the linkages between phenyl radicals being in meta positions relative to each other, the only substituents directly attached to phenyl ring carbon atoms being of the group consisting of hydrogen, tertiary butyl radicals, and alpha-cumyl radicals, and 0.25–2.5% by weight each of bromo-substituted polyphenyl ether, bis(alkylated hydroxyphenyl) sulfide, the alkyl radicals of which has 1–6 carbon atoms each and an indium salt of an aliphatic monocarboxylic acid.
3. As a new lubricating composition a major proportion of polyphenyl ethers having 3–8 phenyl radicals per molecule, the only substituents directly attached to phenyl ring carbon atoms being of the group consisting of hydrogen, tertiary butyl radicals, and alpha-cumyl radicals, said ethers containing 0.25%–2.5% by weight of the indium salt of an alkylated benzoic acid, the benzoic acid nucleus of which bears 1–4 alkyl radicals having 3–10 carbon atoms each.
4. As a new lubricating composition a major proportion of polyphenyl ethers having at least 3 phenyl radicals per molecule, the only substituents directly attached to phenyl ring carbon atoms being of the group consisting of hydrogen, tertiary butyl radicals and alpha-cumyl radicals, said ethers containing 0.25%–2.5% by weight of the indium salt of a thiafatty acid



wherein R₁ is an aliphatic hydrocarbon radical having 4–12 carbon atoms and R₂ is an aliphatic hydrocarbon radical having 1–4 carbon atoms.

5. As a new lubricating composition a major proportion of polyphenyl ethers having 3–8 phenyl radicals per molecule, at least one-third of the linkages between phenyl radicals being in meta positions relative to each other, the only substituents directly attached to phenyl

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ring carbon atoms being of the group consisting of hydrogen, tertiary butyl radicals, and alpha-cumyl radicals, said ethers containing 0.25-2.5% by weight of indium salts of fatty acids having 8-15 carbon atoms per molecule.

6. As a new lubricating composition a major proportion of polyphenyl ethers having at least 3 phenyl radicals per molecule, the only substituents directly attached to phenyl ring carbon atoms being of the group consisting of hydrogen, tertiary butyl radicals, and alpha-cumyl radicals, said ethers containing 0.25-2.5% by weight of at least one indium salt of an acid of the group consisting of fatty acids having 8-15 carbon atoms per molecule, alkylated benzoic acids, the benzoic acid nucleus of which bears 1-4 alkyl radicals having 3-10 carbon atoms each, acids having the general structure



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wherein R_1 is an aliphatic hydrocarbon radical having 4-12 carbon atoms and R_2 is an aliphatic hydrocarbon radical having 1-4 carbon atoms, and mixtures thereof.

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