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POLYPHENYL ETHERS CONTAINING AN EXTREME PRESSURE ADDITIVE

Glenn R. Wilson, Cambridge, and John R. Stemniski, Swampscott, Mass., assignors to Monsanto Research Corporation, St. Louis, Mo., a corporation of Delaware

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This invention relates to lubricating compositions, and more particularly, provides novel lubricating compositions comprising a base fluid and including as an additive a diaminodichlorobenzoquinone.

For lubrication in the temperature range up to 300° or 400° F., mineral oils can be used effectively. However, design requirements in recent years have demanded the development of lubricants effective under conditions of stress, including higher temperatures such as temperatures in the range of 400° or 500° F. up to 1000° F., as well as stress conditions such as ultra-high pressure loads, exposure to ionizing radiation, and the like. Mineral oil compositions cannot meet this demand, and consequently synthetic base fluids have been developed, such as ester and ether base fluids. These oxygenated base fluids have thermal stability superior to the hydrocarbon fluids such as the mineral oils, but on the other hand, their inherent lubricating properties are generally inferior to those of the mineral oils.

In the lubricant art, experience over the years has gradually accumulated a large fund of information on the effect of various types of additives on mineral oils, and it has been found that lubricity can be enhanced by the combination of additives with mineral oil base fluids. However, in development of lubricant compositions based on synthetic base fluids, it has been established that there is no reliable correlation between activity of an additive in a mineral oil and its activity in one of the synthetic base oils. Thus, there is still an unsatisfied demand for the development of compositions useful as functional fluids and particularly as lubricants in the temperature range of 400° or 500° F. and above.

It is an object of this invention to provide novel functional compositions having improved lubricant properties and useful in the temperature range of 400° or 500° F. and above.

It is a particular object of this invention to provide novel high temperature lubricant compositions having improved extreme pressure and anti-wear properties and useful in the temperature range of 400° or 500° F. and above.

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

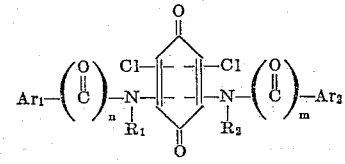
It has now been found that combining a base oil of lubricating viscosity, which remains in the liquid phase up to at least about 500° F., with a diaminodichlorobenzoquinone having an aromatic radical attached to each of the amino nitrogen atoms selected from the class consisting of aryl and arylcarbonyl radicals, provides valuable high temperature lubricant compositions having enhanced lubricating characteristics.

The presently provided lubricant compositions are particularly valuable for the lubrication of moving, frictionally contacting metal surfaces under conditions of stress such as exposure to elevated temperatures, high loads, and the like. It is to be appreciated, however, they are also valuable over a wide spectrum of conditions. As will become evident hereinafter, for example, the presently provided additives decrease the wear exhibited by frictionally contacting metal surfaces even at lower temperatures such as between 100 and 200° F.

In particular, the present invention provides novel, valuable lubricating compositions wherein the stated benzoquinone compounds are combined with a base fluid comprising a polyphenyl ether, such lubricant compositions having superior lubricity characteristics. The polyphenyl ethers are known compounds which have found wide application as functional fluids owing to their very good thermal stability, lubricity, and resistance to foam. For example, they have been found to be valuable as hydraulic fluids, heat exchange media, atomic reactor coolants, diffusion pump fluids, lubricants in motor operation generally, and specifically as jet engine lubricants. The stated polyphenyl ethers may be employed to provide effective lubrication at operating temperatures as high as 600° F. and above, and with the improved compositions comprising such polyphenyl ethers as base fluids in accordance with this invention, good lubrication can be provided even for heavily loaded metal surfaces in frictional contact at such elevated temperatures.

The benzoquinone additives combined with lubricant base fluids to provide lubricant compositions in accordance with this invention are diaminodichlorobenzoquinones wherein an aromatic radical is attached to each amino group, either directly or through a carbonyl group.

In general, they are 1,4-benzoquinones, represented by the formula



where Ar_1 and Ar_2 are aryl radicals, n and m are integers selected from 0 and 1, and R_1 and R_2 are selected from the class consisting of hydrogen, saturated aliphatic hydrocarbon of up to 6 carbon atoms, and a carbonyl group linked to the adjacent aryl radical. The aryl radicals are carbocyclic, benzene or naphthalene, rings linked to the nitrogen atoms, directly or through a carbonyl group, by a ring carbon atom: they may be hydrocarbon or carry any of a wide variety of substituents. This type of compound is readily prepared by condensation of chloranil (tetrachloro-1,4-benzoquinone) with the corresponding aromatic amino, amido or imido compound.

Where the compounds of the invention have an aryl radical directly attached to each amino substituent on the benzoquinone ring, they are dichlorodianilinobenzoquinones and related dichlorodiarylaminobenzoquinones. Thus, illustrative of this type of presently useful additive are

2,5-dichloro-3,6-dianilinobenzoquinone,
2,5-dichloro-3,6-bis(2-methylanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-methylanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-nitroanilino)benzoquinone,
2,5-dichloro-3,6-bis(2,4-dimethylanilino)benzoquinone,
2,5-dichloro-3,6-bis(2,5-dimethylanilino)benzoquinone,
2,5-dichloro-3,6-bis(3-chloroanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-chloroanilino)benzoquinone,
2,5-dichloro-3,6-bis(2-nitroanilino)benzoquinone,
2,5-dichloro-3,6-bis(3-nitroanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-dimethylaminoanilino)benzoquinone,
2,5-dichloro-3,6-bis(2-carboxyanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-carboxyanilino)benzoquinone,
2,5-dichloro-3,6-bis(α-naphthylamino)benzoquinone,
2,5-dichloro-3,6-bis(β-naphthylamino)benzoquinone,
2,5-dichloro-3,6-bis(4-phenylanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-benzylanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-cyclopentylanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-bromoanilino)benzoquinone,
2,5-dichloro-3,6-bis(2,4-dibromoanilino)benzoquinone,
2,5-dichloro-3,6-bis(2,4,6-tribromoanilino)benzoquinone,

2,5-dichloro-3,6-bis(4-methyl-3-nitroanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-bromo-2-nitroanilino)benzoquinone,
2,5-dichloro-3,6-bis(2,4-dibromo-6-nitroanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-acetamidoanilino)benzoquinone,
2,5-dichloro-3,6-bis(2,4,5-trichloroanilino)benzoquinone,
2,5-dichloro-3,6-bis(2,4-dichloroanilino)benzoquinone,
2,5-dichloro-3,6-bis-(4-sulfamylanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-methyl-2-nitroanilino)benzoquinone,
2,5-dichloro-3,6-bis(2-chloro-4-nitroanilino)benzoquinone,
2,5-dichloro-3,6-bis(2,6-dichloro-4-nitroanilino)benzoquinone,
2,5-dichloro-3,6-bis(2-bromo-4-methyl-6-nitroanilino) benzoquinone,
2,5-dichloro-3,6-bis(2-iodoanilino)benzoquinone,
2,5-dichloro-3,6-bis(2-carboxy-5-chloroanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-acetylanilino)benzoquinone,
2,5-dichloro-3,6-bis(2-carbomethoxyanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-sulfo-6-nitro-1-naphthylamino) benzoquinone,
2,5-dichloro-3,6-bis(2-carboxy-3-sulfo-4-chloroanilino) benzoquinone,
2,5-dichloro-3,6-bis(4-diethylaminoanilino)benzoquinone,
2,5-dichloro-3,6-bis(N-methylanilino)benzoquinone,
2,5-dichloro-3,6-bis(N,4-dimethylanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-nitro-N-methylanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-chloro-N-methylanilino)benzoquinone,
2,5-dichloro-3,6-bis(2-chloro-4-nitro-N-methylanilino) benzoquinone,
2,5-dichloro-3,6-bis(N-phenyl-α-naphthylamino)benzoquinone,
2,5-dichloro-3,6-bis(2-chloro-4-nitro-N-methylanilino) benzoquinone,
2,5-dichloro-3,6-bis(N-t-butylanilino)benzoquinone,
2,5-dichloro-3,6-bis(4-nitro-N-t-butylanilino)benzoquinone and so forth.

The presently employed additives wherein a carbonyl group intervenes between the amino substituent of the central benzoquinone ring and the aryl substituent of the amino group are dichlorobis(arylcarboxamido)benzoquinones (N,N' - (dioxodichlorophenylenebis)arylcarboxamides). Thus, illustrative of the presently useful compounds are

2,5-dichloro-3,6-dibenzamido-benzoquinone,
2,5-dichloro-3,6-bis(2-methylbenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-methylbenzamido)benzoquinone,
2,5-dichloro-3,6-bis(2,4-dimethylbenzamido)benzoquinone,
2,5-dichloro-3,6-bis(3-chlorobenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-nitrobenzamido)benzoquinone,
2,5-dichloro-3,6-bis-(4-dimethylaminobenzamido)benzoquinone,
2,5-dichloro-3,6-bis-(2-carboxybenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-carbamyl-benzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-phenylbenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-benzylbenzamido)benzoquinone,
2,5-dichloro-3,6-bis(2,3-dimethylbenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-bromobenzamido)benzoquinone,
2,5-dichloro-3,6-bis(2,4-dibromobenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-methyl-3-nitrobenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-bromo-2-nitrobenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-acetamidobenzamido)benzoquinone,
2,5-dichloro-3,6-bis(2,4-dichlorobenzamido)benzoquinone,

2,5-dichloro-3,6-bis(2-methyl-4-nitrobenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-chloro-2-nitrobenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-benzoylbenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-chlorobenzoylbenzamido)benzoquinone,
2,5-dichloro-3,6-bis(N-methylbenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-nitro-N-methylbenzamido)benzoquinone,
2,5-dichloro-3,6-bis(4-chloro-N-methylbenzamido)benzoquinone,
2,5-dichloro-3,6-bis(2-chloro-4-nitro-N-methylbenzamido) benzoquinone,
2,5-dichloro-3,6-bis(4-nitrobenzamido)-6-benzamidobenzoquinone,
2,5-dichloro-3,6-bis(2,3,5-trichlorobenzamido)-6-(4-nitrobenzamido)benzoquinone.

Further illustrative of an especially preferred embodiment of the presently useful amido-substituted benzoquinone additives are the dichlorophthalimidobenzoquinones. These are exemplified for example by

2,5-dichloro-3,6-diphthalimidozenzoquinone,
2,5-dichloro-3,6-bis(4-nitrophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(4-chlorophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(4-methylphthalimido)benzoquinone,
2,5-dichloro-3-phthalimido-6-benzamidobenzoquinone,
2,5-dichloro-3-(4-nitrophthalimido)-6-phthalimidobenzoquinone,
2,5-dichloro-3,6-bis(3-chlorophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(4-chlorophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(3-nitrophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(4-dimethylaminophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(4-carboxyphthalimido)benzoquinone,
2,5-dichloro-3,6-bis(4-carbamylphthalimido)benzoquinone,
2,5-dichloro-3,6-bis(4-bromophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(2,4-dibromophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(4-methyl-3-nitro-phthalimido)benzoquinone,
2,5-dichloro-3,6-bis(4-bromo-2-nitrophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(3,4-dichlorophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(3-methyl-4-nitrophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(3-methyl-5-nitrophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(3,5-dichlorophthalimido)benzoquinone,
2,5-dichloro-3,6-bis(3-chloro-5-nitrophthalimido)benzoquinone, and the like.

To provide the lubricant compositions of this invention, the benzoquinones of the nature stated above are combined with a high temperature lubricant base fluid. This will be a base oil of lubricating viscosity which remains in the liquid phase at temperatures up to at least about 500° F. In general, the lubricant compositions of this invention will be designed for lubrication of the moving parts of mechanisms operating in temperature ranges of 400° F. to 700° F. A particularly advantageous base fluid for use under these conditions comprises the above-mentioned polyphenyl ethers.

The polyphenyl ethers employed as base fluids 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 pre-

ferred 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, dibiphenylyl 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 Ullman 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 may 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.

The stated synthetic esters are generally aliphatic in nature, as distinguished from the essentially aromatic nature of the polyphenyl ethers, and their properties and response to additives have correspondingly been found to be usually of a different kind. Unexpectedly, however, the presently contemplated quinone additives have been found to provide significant improvement in the properties of the stated ester type of base fluid also. Thus it appears that compositions comprising an adjuvant amount of a quinone as defined above combined with a high temperature lubricant base fluid which, broadly, is an oxygenated carbonaceous base fluid are novel and valuable products with useful properties, and this invention extends to the provision of the stated general class of compositions.

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).

Oxygenated carbonaceous base fluids employed in the present compositions may consist essentially of a polyphenyl ether base fluid alone, a synthetic ester base fluid alone, or a combination of the polyphenyl ether with a synthetic ester base fluid. 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.

A deficiency of the polyphenyl ether base fluids having exceptional thermal and oxidative stability, as exemplified by the bis(phenoxyphenoxy)benzenes discussed above, is lack of fluidity at low temperatures. The fluid range of these materials is unusually wide, encompassing the range from below 100° F. to above 800° F. However, the pour point of certain of these particularly stable fluids is above 0° F., whereas for lubricant use, for example, ability to flow down to temperate climate winter temperatures such as 0° F. is desirable. It has been found that compositions comprising combinations of ester base fluids and the polyphenyl ethers can be provided which have the desired fluidity at low temperatures.

The lubricant fluids which have been found to blend with the phenyl ethers of good thermal and oxidative stability include various esters. It is particularly desirable to provide blends having thermal and oxidative stability at least approaching the stability of the polyphenyl ethers. In this connection, especially valuable base fluids have been found to be provided by combinations of a polyphenyl ether with a neopentyl alcohol ester. These compositions possess both fluidity at low temperature and stability at elevated temperatures.

The preferred polyphenyl ethers for use in this connection are the bis(phenoxyphenoxy)benzenes, of the composition $C_6H_5O—(C_6H_4O—)_3—C_6H_5$ where each C_6H_5 is a phenyl and each C_6H_4 is a phenylene radical. Those with the ether linkages between benzene rings in meta positions, partly or wholly, are especially preferred. The stated neopentyl esters are esters of neopentyl alcohols such as pentaerythritol, trimethylolethane, trimethylolpropane and neopentyl glycol with straight chain, branched chain and mixed C_5—C_{10} acids such as n-heptanoic and neoheptanoic acid.

Compositions of the stated valuable nature and provided by combining 25–75 weight percent of the ester base fluids with 75–25 weight percent of the polyphenyl ethers.

As noted hereinabove, additive activity and particularly lubricity-improving additive activity is usually not found to be general to different classes of lubricant base fluids. However, as will appear from the examples hereinafter, compositions comprising the presently employed benzoquinones have unexpectedly been found to possess improved properties compared to the base stock alone with base oils of diverse kinds. So far as is known, the presently provided compositions, consisting essentially of a benzoquinone of the above-described nature and a base oil of lubricating viscosity which remains in the liquid phase at least up to about 500° F., are novel materials. Thus in its broader aspects, this invention relates to provision of compositions of the stated scope, using various base stocks of the stated description. For example, the base stock may be a hydrocarbon oil, a silicon-containing oil, a fluorinated oil, and so forth.

Illustrative of contemplated hydrocarbon lubricant base fluids are the aromatic hydrocarbons, particularly condensed ring structures such as biphenyl, alkylbiphenyls such as isopropylbiphenyl, and terphenyls, quarterphenyls, the alkyl derivatives of these polyphenyls such as dimethyl terphenyl, and the like. Hydrogenated derivatives of these aromatic hydrocarbons, including alicyclic rings and alkylated alicyclic rings, have also been observed to possess fair stability under high temperature stress conditions. Mineral oils, paraffinic and naphthenic, can also be provided with substantially improved high temperature stability as compared to the less refined oils in common use under less severe conditions, by super-refining. Super-refining is the removal or substantial reduction of the polar impurities, unsaturates and unstable hydrocarbon structures by exhaustive hydrogenation, severe acid treatment, adsorption, or a combination of these processes. The effects include improvement in thermal stability and metal corrosion tendencies dirt formation and pressure buildup due to decomposition as compared to conventionally refined mineral oils. Oxidation rates at 500° F. are approximately the same for the super-refined mineral oils as for the ester lubricants. Useful mineral oils for lubricant compositions are, as is known in the art, the petroleum products boiling at temperatures above the kerosene range. A typical mineral oil base for extreme pressure lubrication will be characterized by a viscosity of 35–350 Saybolt Universal seconds at 212° F., a viscosity index in the range of from −25 to +150 and a flash point of between about 275° and 600° F.

Silicon-base high-temperature lubricant fluids are exemplified, for example, by silanes such as n-dodecyl tri-n-decyl silane and diphenyl di-n-dodecyl silane; the silicone polymer fluids such as dimethyl silicone and methyl phenyl silicone polymers, and disiloxanes and tetraalkyl orthosilicate esters such as di-tert-butyl di-2-ethylhexyl orthosilicate, 1,3-di-tert-butoxy-1,1,2,2-tetra(2-pentoxy) disiloxane, tetra(methylphenyl) silicate, tetraphenyl silicate, tetra(2-ethylhexyl) silicate, and so forth.

Illustrative of fluorine containing base fluids are fluorinated esters like bis(perfluoroamyl)phthalate, bis(perfluorohexyl) 3-methyl glutarate, and 1,1-H-nonafluoropentyl nonafluoropentanoate; and the polymers of chlorotrifluoroethylene, for example, with average molecular weights of about 500–1000, and so forth.

The compositions of this invention will consist essentially of a major proportion of the base fluid and a minor proportion of the benzoquinone additive. In general, when the ultimate formation of the base fluid to be introduced into the equipment to be lubricated has been made, the concentrations to be employed for effective improvement of the base fluid properties by the benzoquinone additive will be generally between about 0.01% and 10.0% by weight. The precise quantity will depend on the nature of the adjuvant compound and of the base fluid, and upon the adjuvant effect desired. Thus the most effective concentration for diminishing wear of moving metal parts and that for increasing the pressure load which the lubricated parts can exert without seizure may not be the same. In any case, at least an adjuvant amount sufficient to produce an improvement in at least one of the lubricant properties of the base fluid will be employed. Whether or not the desired adjuvant effect is obtained is readily determined by use of conventional testing procedures known to those skilled in the art.

It is frequently beneficial to employ a combination of different additives in formulating ultimate lubricant compositions. For example, nitrogenous compounds such as phenothiazine and derivatives thereof are often employed to increase oxidation resistance, and polymeric materials such as polyacrylic esters may be employed as viscosity index improvers, sludge dispersants, and so forth. It is to be appreciated that such additional beneficial additive may and desirably will be present in lubricant compositions embodying the present invention.

In the following examples, the tests employed to determine the reported adjuvant effects of the quinone compounds when employed with the lubricant base fluids are conducted as follows:

The anti-wear and extreme pressure lubrication characteristics of the lubricant compositions are evaluated by

means of the "Shell 4-Ball Extreme Pressure Tester" and the "Shell 4-Ball Wear Machine." These testers include four balls of stainless steel arranged in the form of an equilateral tetrahedron. The three lower balls are held immovably clamped in a holder to form a cradle in which the fourth upper ball is caused to rotate at 1200–1800 r.p.m. about a vertical axis in contact with the three lower stationary balls. The contacting surfaces of the balls are immersed in the test fluid, which is held in a cup surrounding the assembly. A modified cup and heater assembly is used to evaluate lubricants at elevated temperature and provisions are made to permit testing under an inert atmosphere: see "The Study of Lubrication Using the Four Ball Type Machine," by R. G. Larsen, Lubrication Engineering, vol. I, pages 35–43, 59 (August 1945).

For measurement of wear, the rotating ball is rotated under a load of 40 kilograms (kg.) for 1 hour at each of the temperatures for which wear scar diameters worn in the surface of the three lower stationary balls are reported.

For determination of the extreme pressure properties in the 4-Ball EP Tester, the upper ball is rotated while the load is gradually increased by increments of 10 kg. until the balls are welded together in a 1 minute test period.

Additionally, the present compositions have been submitted to the Falex antiweld test: see the articles by V. A. Ryan in "Lubrication Engineering" September 1946 and by S. Kyropoulos in "Refiner Natural Gasoline Manufacturer," vol. 18, pages 320–24 (1939), and Amer. Soc. Test. Matls. D–2, Section V, Tech. K. A steel journal pin is rotated by a driving shaft at 290 r.p.m. in jaws (V-bearing steel blocks) through which a constantly increasing load is applied, with ratchet means compensating for wear of the journal pin during the test. The assembly is immersed in the lubricant. The load at failure due either to seizure or to wear at a rate faster than the load-increasing rate is recorded.

Example 1

A lubricant composition is prepared by combining 2,5-dianilino-3,6-dichloro-1,4-benzoquinone with a polyphenyl ether of the following composition, by weight:

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

in a proportion of 1 gram (g.) of the quinone to 100 of the base fluid.

A portion of the base fluid used to provide the above-described composition is reserved, free of additive, and run through the same sequence of tests, to provide a basis for comparison.

Using the base fluid alone, in the extreme pressure test, the balls weld at a pressure of 150 kg.

Employing the lubricant composition described above consisting of 1% of the quinone compound combined with the same polyphenyl ether, the weld point found is 490 kg.

Using the Shell 4-Ball Wear Tester, the wear scar diameters determined for the lubricant composition of this example including the stated quinone and for the base fluid without additive are as follows:

	Wear Scar Diameter, mm.	
	167° F.	600° F.
With additive	1.45	1.71
Without additive	1.82	2.92

Example 3

A lubricant composition is prepared by combining 2,5-bis(4-nitrophthalimido)-3,6-dichloro-1,4 - benzoquinone with a polyphenyl ether base fluid of the composition stated in Example 1, in a concentration of 1 g. per 100 g.

The solution of the additive in the polyphenyl ether is subjected to test of its extreme pressure and wear properties in the Shell 4-Ball Testers, with results as follows:

	Weld Point, kg.	Wear Scar Diameter, mm.	
		167° F.	600° F.
With additive	400	1.45	2.05
Without additive	150	1.82	2.92

Example 3

This example further illustrates the increase in load-carrying ability of the polyphenyl ether base stock in the presently provided compositions including quinonic additives.

The method of test employed is the above-described Falex Shear Load Test. Three samples are run in this tester; in each sample, the base stock is the polyphenyl ether base stock described in Example 1:

(1) The base stock, free of additive;

(2) The base stock, plus 1.0 gram (g.) per 100 g. base stock, of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone;

(3) The base stock plus 1.0 g., per 100 g. of base stock, of 2,5-bis(4-nitrophthalimido)-3,6 - dichloro - 1,4-benzoquinone.

The average failure load of the base stock without additive is 500, whereas for each of compositions (2) and (3) with quinonic additives included, it is 2500.

Example 4

This example describes preparation and properties of a lubricant composition which is a solution of a dichlorodiaminoquinone in an oxygen-containing base fluid of the ester type.

A saturated solution is prepared of 2,5-dichloro-3,6-bis(o-chloroanilino)-1,4-benzoquinone in trimethylolpropane trienanthate, containing a concentration of about 0.75 g. of the quinone per 100 g. of the base fluid.

For evaluation of the ability of the additive to increase the load-carrying ability of the base stock and improve wear characteristics, the tests employed are the Shell 4-Ball Extreme Pressure and Shell 4-Ball Wear Test described above. In the extreme pressure test, the weld point of the base stock without additive is 130 kg., while the weld point for the composition in which the base stock contains the dissolved quinone compound is 210 kg. Measurement of the wear scar diameter gives values of approximately 1 mm. at 167° and at 400° F. (1.07 and 1.03 mm. respectively), whereas for the ester without additive, the 400° F. wear scar diameter is 2.29 mm.

Example 5

This example describes lubricating characteristics of compositions consisting of a mineral oil and a quinone in accordance with the invention.

Lubricant compositions are provided by dissolving 2,5-dichloro-3,6-bis(o-chloroanilino)-1,4-benzoquinone in a naphthenic white oil described as MLO–7357, which has a pour point of −18° F., viscosity 80.57 cps. at 100° F., 8.51 cps. at 210° F., to the limit of the room temperature solubility of the quinone in the oil, producing a concentration of about 0.25 g. per 100 g. of base oil.

Without additive, this oil has a weld point of 120 kg. and produces wear scar diameters of 1.73 mm. at 167° F. and 3.57 at 400° F. The composition comprising the stated quinone has a weld point of 210–220 kg. and the wear scar diameter is 0.83 mm. at 167° F. and 1.0 mm. at 400° F.

While the invention has been described with reference to specific 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 defined in the appended claims.

What is claimed is:

1. A composition consisting essentially of (1) a major amount of a base oil of lubricating viscosity which remains in the liquid phase up to at least about 500° F., and (2) a diaminodichlorobenzoquinone having an aromatic radical attached to each of the amino nitrogen atoms selected from the class consisting of aryl and arylcarbonyl radicals, in an amount sufficient to improve the extreme pressure and anti-wear characteristics of said base oil.

2. The composition of claim 1 wherein said base oil is selected from the class consisting of polyphenyl ether and synthetic ester base fluids.

3. The composition of claim 2 wherein said benzoquinone is a di(arylamino)dichloro-1,4-benzoquinone.

4. The composition of claim 3 wherein said benzoquinone is 2,5-dichloro-3,6-bis(o-chloroanilino)benzoquinone.

5. The composition of claim 2 wherein said base oil comprises a polyphenyl ether base fluid.

6. A functional fluid composition consisting essentially of a polyphenyl ether base fluid consisting of from 3 to 7 benzene rings joined in a chain by oxygen atoms as ether linkages between each ring, and an amount of a di(arylamino)dichloro-1,4-benzoquinone sufficient to improve a lubricating characteristic of the polyphenyl ether base fluid selected from the group consisting of extreme pressure and anti-wear characteristics.

7. The composition of claim 6 wherein said benzoquinone is 2,5-dichloro-3,6-dianilino-1,4-benzoquinone.

8. The composition of claim 7 in which the said polyphenyl ether base fluid consists of a mixture of bis(phenoxy-phenoxy)benzenes.

9. The composition of claim 2 wherein said benzoquinone is a bis(arylcarbonyl-substituted-amino)dichloro-1,4-benzoquinone.

10. A functional fluid composition in which the base fluid comprises a major amount of a polyphenyl ether consisting of from 3 to 7 benzene rings joined in a chain by oxygen atoms as ether linkages between each ring, and an amount of a bis(arylcarbonyl-substituted-amino)dichloro-1,4-benzoquinone sufficient to improve a lubricating characteristic of said polyphenyl ether base fluid selected from the class consisting of extreme pressure and anti-wear characteristics.

11. The composition of claim 10 in which said benzoquinone is 2,5-dichloro-3,6-bis(4-nitrophthalimido)-1,4-benzoquinone.

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DANIEL E. WYMAN, *Primary Examiner.*