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(54) **FLUOROCARBON SEAL PROTECTIVE ADDITIVES FOR LUBRICATION OILS**

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ADDITIFS PROTEGEANT LES JOINTS D'ETANCHEITE AU FLUOROCARBONE DESTINES AUX HUILES DE GRAISSAGE

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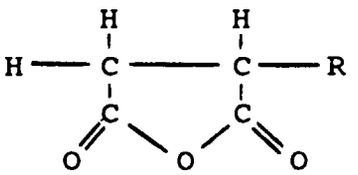
Description

FIELD OF THE INVENTION

This invention relates to a discovery that a borated aromatic polyol having at least one aromatic ring and at least two hydroxyl groups and wherein at least two of the hydroxyl groups are on adjacent carbon atoms on the aromatic ring can serve to inhibit fluorocarbon engine seal deterioration in the presence of basic nitrogen.

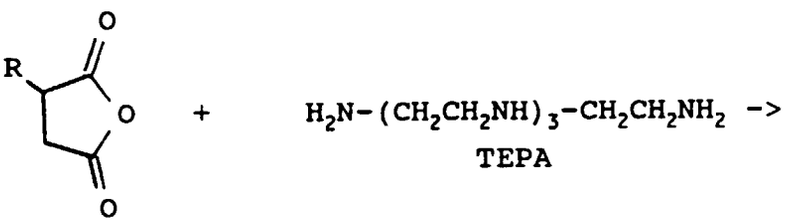
BACKGROUND

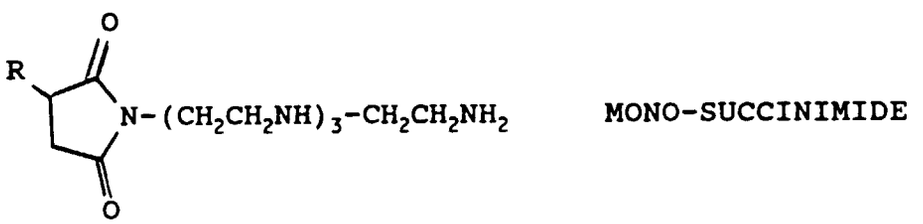
The most important automotive lubricating formulations are based on using dispersants as additives. One of the most effective dispersants in use today is based on succinic anhydride with a long polyisobutylene alkyl chain in the alpha position, i.e.:



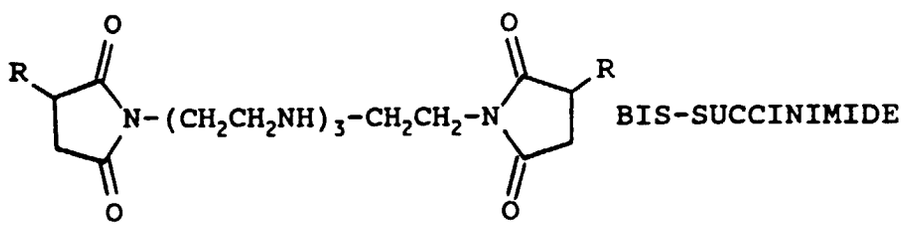
where R is a polyisobutylene.

These succinic anhydrides are then reacted with a polyamine, such as tetraethylenepentamine (TEPA) or triethylenetetramine (TETA), in a certain mole ratio to give predominantly either a mono- or bis-succinimide, i.e.:





and/or



These, and other additives, such as Mannich bases, have basic nitrogen (Total Base Number (TBN) of 28-45, generally measured as mg KOH/g sample), and are used to protect the metallic parts of the engine while in service from acidic components formed as the result of the oxidation of oil and fuel, and to keep the high molecular weight oxidation products and sludge precursors dispersed in the oil, and thus minimize their agglomerization.

While basicity (as evidenced by TBN) is an important property to have in the dispersant additive, it is also believed that the initial attack on the fluorocarbon elastomer seals used in some engines involves attack by the basic nitrogen which leads to the loss of fluoride ions, and eventually results in cracks in the seals, and loss of other desirable physical properties in the elastomer. One approach towards solving the elastomer problem is to use a bis-succinimide instead of mono-succinimide, in essence, diluting the basic nitrogen content level of the dispersant. However, as will be shown later in the Examples, even the bis-succinimides alone will not serve to pass the fluorocarbon seal bench test.

In practice, a mixture of mono- and bis-succinimides is used, usually predominating in the latter. Thus, additional means are necessary to inhibit the deterioration of the fluorocarbon seals in the presence of additives containing basic nitrogen.

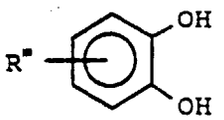
U.S.P. 4,873,009, issued October 10, 1989, to Ronald L. Anderson and entitled, "Borated Lube Oil Additive", is also concerned, in part, with the use of succinimides as lube oil additives. Anderson recognizes in Col. 2, lines 28 et seq. that lube additives prepared from "long chain aliphatic polyamines", i.e.,succinimides "are excellent lube oil additives." However, Anderson teaches such succinimides are "inferior to additives where the alkylene polyamine is hydroxylated" (Col.2, lines 31 - 32). Such hydroxylated polyamine based succinimides "have the drawback that they tend to attack engine seals particularly those of the fluorocarbon polymer type" (Col. 2, lines 35-37).

Anderson solves his fluorocarbon polymer seal compatibility problem by directly borating his hydroxylated polyamine based succinimides. Anderson fails to teach or suggest any solution to the fluorocarbon seal compatibility problem when using unhydroxylated polyamine based succinimides. In fact, Anderson teaches that boration of the unhydroxylated succinimides failed to solve the problem (Col. 3, lines 3 to 5). What is desired and needed is a separate additive to use with other lube oil additives containing basic nitrogen which will serve to inhibit the deterioration of engine seals of the fluorocarbon polymer type.

SUMMARY OF THE INVENTION

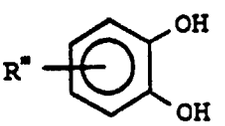
In accordance with the invention, an additive has now been discovered which will improve the compatibility of lubricating oils containing basic nitrogen towards fluorocarbon engine seals.

According to a first aspect of the present invention there is provided the use of a borated aromatic polyol, in a lubricating composition containing a minor proportion of a basic nitrogen compound, for the purpose of improving the compatibility of said lubricating oil towards fluorocarbon polymer engine seals, said borated aromatic polyol being obtainable by borating an aromatic polyol having the formula:



where R''' is selected from the group consisting of H; OH; or an alkyl group having from 1 to 8 carbon atoms. The borated aromatic polyol is used at an effective amount to improve the compatibility of the lubricating oil towards fluorocarbon engine seals.

According to a second aspect of the present invention, there is provided a lubricant composition comprising a major proportion of a lubricating oil; a minor proportion of at least one basic nitrogen compound and a minor but effective compatibilizing amount of a borated aromatic polyol as an additive to passavate fluorocarbon polymer seals, said aromatic polyol being obtainable by borating an aromatic polyol having the formula:



wherein R''' is selected from the group consisting of H; OH; or an alkyl group having from 1 to 8 carbon atoms. Usually

the basic nitrogen content of the lubricating oil is provided through the use of an oil soluble alkyl or alkenyl mono- or bis-succinimide. The borated aromatic polyol, such as borated catechol, is believed to complex with the basic nitrogen.

The complexation of borated long-chain alkyl catechols with succinimides (which contain basic nitrogen) is described in U.S.P. 4,629,578 to T. V. Liston. Liston teaches in Col. 1, lines 21 et seq., that the use of borated alkyl catechols in lube oils is known for anti-oxidation purposes. But, the borated alkyl catechols are sensitive to moisture and hydrolyze readily. Liston teaches complexing the borated alkyl catechols with succinimides to stabilize the catechols against hydrolysis (Col. 1, lines 32-35).

The borated alkyl catechols of Liston are those where the alkyl group has from 10 to 30 carbon atoms (Col. 2, lines 22 et seq.).

Other additives may also be present in the lubricating oil in order to obtain a proper balance of properties such as dispersancy, corrosion, wear and oxidation inhibition which are critical for the proper operation of an internal combustion engine.

In still another aspect of this invention, there is provided a method for improving the compatibility of a lubricating oil containing basic nitrogen to fluorocarbon seals in engines which comprises adding to said lubricating oil a compatibilizing amount of the borated aromatic polyols of this invention.

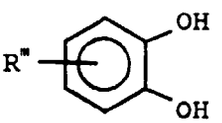
BRIEF DESCRIPTION OF THE FIGURE

The Figure is a graphic representation of the change in dispersion units of a reference oil containing a alkylcatechol borate versus the number of carbon atoms inthe alkyl group of the alkylcatechol borate.

DETAILED DESCRIPTION OF THE INVENTION

The aromatic polyol for use in the invention is a single ring aromatic having from 2 to 3 hydroxyl groups and wherein two of the hydroxyl groups are on adjacent carbon atoms on the aromatic ring.

Thus, the aromatic polyols used in the invention are those having the formula:



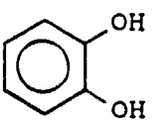
where R''' is selected from the group consisting of H; OH; or an alkyl group having from 1 to 8, preferably 1 to 6 and more preferably 1 to 4 carbon atoms.

While all catechol borates, as the data later show, can be expected to compatibilize the oil with the fluorocarbon polymer seals, catechol borates without any alkyl groups, or those carrying a short chain alkyl group of 1-8 carbons, were unexpectedly found by the dispersancy blotter spot test, to be discussed later, to be effective in enhancing the overall dispersancy, while alkylcatechol borates carrying long alkyl groups surprisingly showed a loss in the overall dispersancy.

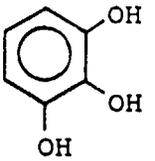
Also, mixtures of aromatic polyols as described above can be employed, the higher carbon number alkylated catechols tending to solubilize the lower molecular weight catechols in the lubricating oil.

For example, one of the shortcomings of using catechol borate is that its solubility in the reference oil formulation at room temperature is limited, in spite of its excellent dispersancy characteristic. It has now been discovered that alkylcatechol borates having an alkyl group of ten carbon atoms or longer can be used effectively to enhance the solubility of catechol borate in a reference oil, and the overall loss in dispersancy of the higher alkylcatechol borates can be offset by the addition of the lower alkylcatechol borate or catechol borate which has a positive effect on the overall dispersancy. The most effective ratio to use for optimum results is a matter of simple experimentation.

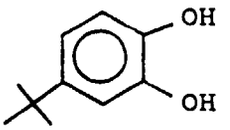
Examples of aromatic polyols which can be used to prepare the borated aromatic polyols for use in this invention include, but are not limited to:

Catechol 

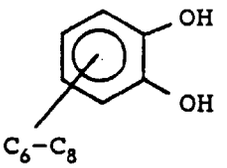
Pyrogallol



4-tertiary butyl catechol



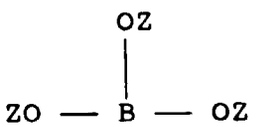
Alkyl (C_6-C_8) catechol



The aromatic polyols useful in preparing the additives of this invention are well known in the art and many are commercially available. The alkyl catechols may be prepared, for example, as described in U.S.P. 4,629,578.

The aromatic polyols are borated by methods well known in the art, see for example U.S.P. 4,975,211 and U.S.P. 4,629,578. The preferred boron compound to employ in the boration reaction is boric acid. The borated compounds used in the working examples in this application were either prepared via published procedures in U.S.P. 4,975,211; and U.S.P. 4,629,578, or were purchased from commercial sources.

It is believed that a boron compound with a labile hydrogen is necessary to borate the aromatic polyols of this invention. A preferred boron source would have the formula:

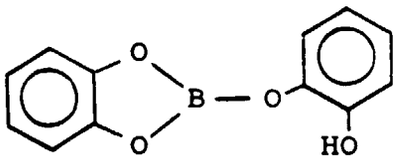


where Z can be hydrogen or an alkyl group having 1 to 20 carbon atoms, preferably 1 to 8. Preferred is boric acid ($B(OH)_3$).

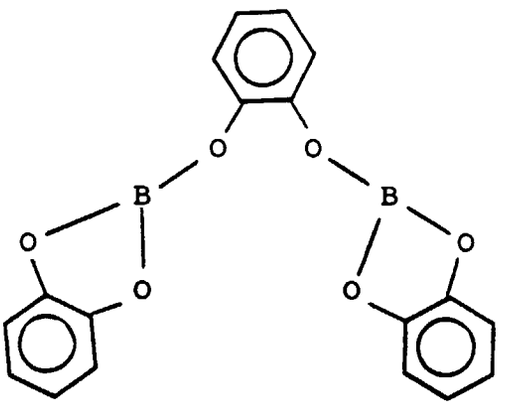
The simplest borated aromatic polyol to use in the compositions of this invention is catechol borate.

Catechol borate is a general term which has been used in the literature to describe any catechol-boric acid complex or reaction product. The exact structure of the product, however, is dictated largely by stoichiometry (charge molar ratio of reactants). The extent of the reaction is most conveniently followed by the amount of water of reaction collected in a Dean-Stark trap using some appropriate organic azeotroping solvent such as toluene, o-xylene, m-xylene, p-xylene, xylene mixture, and etc. All of catechol-boric acid structures are known from the literature and are shown in Table A below. For example, when the molar ratio of catechol to boric acid is 2:1, the major product was expected to have structure I. At a molar ratio of 3:2, the major product was expected to have structure II. And finally, at a stoichiometric ratio of 1:1, the major product was expected to have structure III initially, but on continued heating, the expected product should have structure IV. In a real world situation, all structures I-IV, as well as the unreacted catechol, are probably present in every product mixture, but in different amounts depending on the stoichiometry employed and the equilibrium phenomenon.

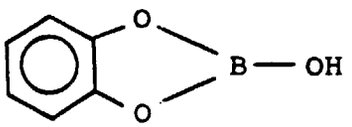
TABLE A



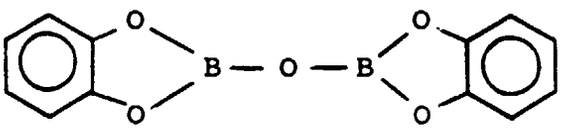
Structure I



Structure II



Structure III



Structure IV

The amount of the borated aromatic polyol to use in the compositions of this invention is that amount which is sufficient to improve the compatibility of the basic nitrogen containing additives in the lube oil base stock towards fluorocarbon engine seals.

In general, the amount of borated aromatic polyol to add is at least the stoichiometric amount required to react or to passivate the basic nitrogen atoms present, although depending on the circumstances, the amount of boron added can be greater or less than the stoichiometric amount of available basic nitrogen. When less than the stoichiometric amount of boron was used, the full benefit of boron containing additives may not be reached, and the results may not

be optimum. Usually the weight percent of said borated aromatic polyol is at least about 0.15 weight percent of the lube oil composition, more usually 0.5 to 5 weight percent although amounts to 10 weight percent or more can be used.

The borated aromatic polyols of this invention are useful in complexing with basic nitrogen in the lubricating oil so as to compatibilize the lubricating oil with the fluorocarbon seals. By "compatibilize" is meant that the basic nitrogen is passivated against attack on the fluorocarbon seals. Compatibility is measured by a pass rating on a VW Bench Test developed by Volkswagen and known in the industry as PV3334 bench test, carried out in accordance with the DIN 53504 procedure, which will be described in detail below using a standard reference elastomer AK6 from Parker-Pradifa GmbH of 2mm thickness (S2 specimen).

It is well known that organic amines containing basic nitrogen attack fluorocarbon seals (See, for example, U.S. P. 4,873,009 described above; and Effects of Organic Amine Inhibitors on Elastomers in Elastomerics, September 1986, pages 24-27). Fluorocarbon elastomers or rubbers are also well known and are sold, for example, by the DuPont Company under the tradename "Viton®" fluoroelastomer (see "The Effect of Lubricating Oil Additives on the Properties of Fluorohydrocarbon Elastomers", by A. Nersasian of DuPont in Preprint No. 79-AM-3C-3 of American Society of Lubricating Engineers for a description of elastomers and the effect of various additives).

The oil soluble alkenyl or alkyl mono- or bis-succinimides which are employed in this invention are generally known as lubricating oil detergents and are described in U.S. Pat Nos. 2,992,708, 3,018,291, 3,024,237, 3,100,673, 3,219,666, 3,172,892 and 3,272,746. The alkenyl succinimides are the reaction product of a polyolefin polymer-substituted succinic anhydride with an amine, preferably a polyalkylene polyamine. The polyolefin polymer-substituted succinic anhydrides are obtained by reaction of a polyolefin polymer or a derivative thereof with maleic anhydride. The succinic anhydride thus obtained is reacted with the amine compound. The preparation of the alkenyl succinimides has been described many times in the art. See, for example, U.S. Pat. Nos. 3,390,082, 3,219,666 and 3,172,892. Reduction of the alkenyl substituted succinic anhydride yields the corresponding alkyl derivative. A product comprising predominantly mono- or bis-succinimide can be prepared by controlling the molar ratios of the reactants. Thus, for example, if one mole of amine is reacted with one mole of the alkenyl or alkyl substituted succinic anhydride, a predominantly mono-succinimide product will be prepared. If two moles of the succinic anhydride are reacted per mole of polyamine, a bis-succinimide will be prepared.

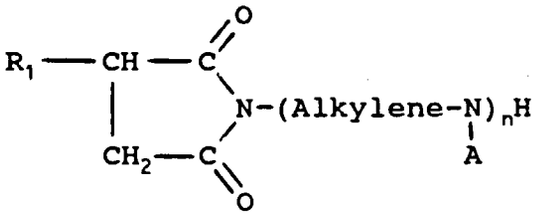
Particularly good results with the lubricating oil compositions of this invention are obtained when the alkenyl succinimide is a mono- or a bis-succinimide prepared from a polyisobutene-substituted succinic anhydride of a polyalkylene polyamine.

The polyisobutene (from which the polyisobutene-substituted succinic anhydride is prepared) is obtained by polymerizing isobutene and can vary widely in its composition. The average number of carbon atoms can range from 30 or less to 250 or more, with a resulting number average molecular weight of about 400 or less to 3,000 or more. Preferably, the average number of carbon atoms per polyisobutene molecule will range from about 50 to about 100 with the polyisobutene having a number average molecular weight of about 600 to about 1,500. More preferably, the average number of carbon atoms per polyisobutene molecule ranges from about 60 to about 90, and the number average molecular weight ranges from about 800 to 1,300. The polyisobutene is reacted with maleic anhydride according to well-known procedures to yield the polyisobutene-substituted succinic anhydride. See, for example, U.S. Pat. Nos. 4,388,471 and 4,450,281.

In preparing the alkenyl succinimide, the substituted succinic anhydride is reacted with a polyalkylene polyamine to yield the corresponding succinimide. Each alkylene radical of the polyalkylene polyamine usually has up to about 8 carbon atoms. The number of alkylene radicals can range up to about 8. The alkylene radical is exemplified by ethylene, propylene, butylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, octamethylene, etc. The number of amino groups generally, but not necessarily, is one greater than the number of alkylene radicals present in the amine, i.e., if a polyalkylene polyamine contains 3 alkylene radicals, it will usually contain 4 amino radicals. The number of amino radicals can range up to about 9. Preferably, the alkylene radical contains from about 2 to about 4 carbon atoms and all amine groups are primary or secondary. In this case, the number of amine groups exceeds the number of alkylene groups by 1. Preferably the polyalkylene polyamine contains from 3 to 5 amine groups. Specific examples of the polyalkylene polyamines include ethylenediamine, diethylenetriamine, triethylenetetramine, propylenediamine, tripropylenetetramine, tetraethylenepentamine, trimethylenediamine, pentaethylenehexamine, di-(trimethylene)triamine, tri(hexamethylene)tetramine, etc.

Other amines suitable for preparing the alkenyl succinimide useful in this invention include the cyclic amines such as piperazine, morpholine and dipiperazines.

Preferably the alkenyl succinimides used in the compositions of this invention have the following formula:



wherein:

a. R_1 represents an alkenyl group, preferably a substantially saturated hydrocarbon prepared by polymerizing aliphatic monoolefins and preferably R_1 is prepared from isobutene and has an average number of carbon atoms and a number average molecular weight as described above;

b. the "Alkylene" radical represents a substantially straight chain hydrocarbyl group containing up to about 8 carbon atoms and preferably containing from about 2 to 4 carbon atoms as described hereinabove;

c. "A" represents a hydrocarbyl group, an amine-substituted hydrocarbyl group, or hydrogen; the hydrocarbyl group and the amine-substituted hydrocarbyl groups are generally the alkyl and amino-substituted alkyl analogs of the alkylene radicals described above; and preferably "A" represents hydrogen; and

d. n represents an integer of from about 1 to 10, and preferably from about 3 to 5 inclusive.

The alkenyl succinimide is present in the lubricating oil compositions useful in this invention in an amount sufficient to impart the desired dispersant properties to the lubricating oil to prevent the deposit of contaminants formed in the oil during operation of the engine. In general, the weight percent succinimide is from 1 to 20 weight percent of the finished lubricating oil, usually from 2 to 15 weight percent and preferably from 1 to 10 weight percent of the total composition.

The addition of the borated aromatic polyols described above to the alkenyl succinimide results in the formation of a complex with the succinimide.

The exact structure of the complex of this invention is not known for certain. However, while not limiting this invention to any theory, it is believed to be compounds in which boron is either complexed by, or is the salt of, one or more nitrogen atoms of the basic nitrogen contained in the succinimide. Therefore, in most cases the alkenyl succinimide will contain at most 5, but preferably 2 to 3 basic nitrogens per succinimide.

The complex may be formed by reacting the borated alkyl catechol and the succinimide together neat at a temperature above the melting point of the mixture of reactants and below the decomposition temperature, or in a diluent in which both reactants are soluble. For example, the reactants may be combined in the proper ratio in the absence of a solvent to form a homogeneous product which may be added to the oil or the reactants may be combined in the proper ratio in a solvent such as toluene or chloroform, the solvent stripped off, and the complex thus formed may be added to the oil. Alternatively, the complex may be prepared in a lubricating oil as a concentrate containing from about 20 to 90% by weight of the complex, which concentrate may be added in appropriate amounts to the lubricating oil in which it is to be used or the complex may be prepared directly in the lubricating oil in which it is to be used.

The diluent is preferably inert to the reactants and products formed and is used in an amount sufficient to ensure solubility of the reactants and to enable the mixture to be efficiently stirred.

Temperatures for preparing the complex may be in the range of from 25°C to 200°C and preferably 25°C to 100°C depending on whether the complex is prepared neat or in a diluent, i.e., lower temperatures may be used when a solvent is used.

In general, the complexes of this invention may also be used in combination with other additive systems in conventional amounts for their known purpose.

For example, for application in modern crankcase lubricants, the base composition described above will be formulated with supplementary additives to provide the necessary stability, detergency, dispersancy, anti-wear and anti-corrosion properties.

Thus, as another embodiment of this invention, the lubricating oils to which the complexes prepared by reacting the borated alkyl catechols and succinimides may contain an alkali or alkaline earth metal phenate, and Group II metal salt dihydrocarbyl dithiophosphate.

Also, since the succinimides act as excellent dispersants, additional succinimide may be added to the lubricating

oil compositions, above the amounts added in the form of the complex with the borated alkyl catechols. The amount of succinimides can range up to about 20% by weight of the total lubricating oil compositions.

The alkali or alkaline earth metal hydrocarbyl sulfonates may be either petroleum sulfonate, synthetically alkylated aromatic sulfonates, or aliphatic sulfonates such as those derived from polyisobutylene. One of the more important functions of the sulfonates is to act as a detergent and dispersant. The sulfonates are well known in the art. These hydrocarbyl group must have a sufficient number of carbon atoms to render the sulfonate molecule oil soluble. Preferably, the hydrocarbyl portion has at least 20 carbon atoms and may be aromatic or aliphatic, but is usually alkylaromatic. Most preferred for use are calcium, magnesium or barium sulfonates which are aromatic in character.

Certain sulfonates are typically prepared by sulfonating a petroleum fraction having aromatic groups, usually mono- or dialkylbenzene groups, and then forming the metal salt of the sulfonic acid material. Other feedstocks used for preparing these sulfonates include synthetically alkylated benzenes and aliphatic hydrocarbons prepared by polymerizing a mono- or diolefin, for example, a polyisobutenyl group prepared by polymerizing isobutene. The metallic salts are formed directly or by metathesis using well-known procedures.

The sulfonates may be neutral or overbased having base numbers up to about 44 or more. Carbon dioxide and calcium hydroxide or oxide are the most commonly used material to produce the basic or overbased sulfonates. Mixtures of neutral and overbased sulfonates may be used. The sulfonates are ordinarily used so as to provide from 0.3% to 10% by weight of the total composition. Preferably, the neutral sulfonates are present from 0.4% to 5% by weight of the total composition and the overbased sulfonates are present from 0.3% to 33% by weight of the total composition.

The phenates for use in this invention are those conventional products which are the alkali or alkaline earth metal salts of alkylated phenols. One of the functions of the phenates is to act as a detergent and dispersant. Among other things, it prevents the deposit of contaminants formed during high temperature operation of the engine. The phenols may be mono- or polyalkylated.

The alkyl portion of the alkyl phenate is present to lend oil solubility to the phenate. The alkyl portion can be obtained from naturally occurring or synthetic sources. Naturally occurring sources include petroleum hydrocarbons such as white oil and wax. Being derived from petroleum, the hydrocarbon moiety is a mixture of different hydrocarbyl groups, the specific composition of which depends upon the particular oil stock which was used as a starting material. Suitable synthetic sources include various commercially available alkenes and alkane derivatives which, when reacted with the phenol, yield an alkylphenol. Suitable radicals obtained include butyl, hexyl, octyl, decyl, dodecyl, hexadecyl, eicosyl, triacontyl, and the like. Other suitable synthetic sources of the alkyl radical include olefin polymers such as polypropylene, polybutylene, polyisobutylene and the like.

The alkyl group can be straight-chained or branch-chained, saturated or unsaturated (if unsaturated, preferably containing not more than 2 and generally not more than 1 site of olefinic unsaturation). The alkyl radicals will generally contain from 4 to 30 carbon atoms. Generally when the phenol is monoalkyl-substituted, the alkyl radical should contain at least 8 carbon atoms. The phenate may be sulfurized if desired. It may be either neutral or overbased and if overbased will have a base number of up to 200 to 300 or more. Mixtures of neutral and overbased phenates may be used.

The phenates are ordinarily present in the oil to provide from 0.2% to 27% by weight of the total composition. Preferably, the neutral phenates are present from 0.2% to 9% by weight of the total composition and the overbased phenates are present from 0.2 to 13% by weight of the total composition. Most preferably, the overbased phenates are present from 0.2% to 5% by weight of the total composition.

Preferred metals are calcium, magnesium, strontium or barium.

The sulfurized alkaline earth metal alkyl phenates are preferred. These salts are obtained by a variety of processes such as treating the neutralization product of an alkaline earth metal base and an alkylphenol with sulfur. Conveniently the sulfur, in elemental form, is added to the neutralization product and reacted at elevated temperatures to produce the sulfurized alkaline earth metal alkyl phenate.

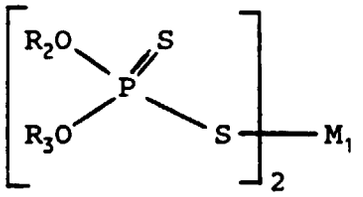
If more alkaline earth metal base were added during the neutralization reaction than was necessary to neutralize the phenol, a basic sulfurized alkaline earth metal alkyl phenate is obtained. See, for example, the process of Walker et al., U.S. Pat. No. 2,680,096. Additional basicity can be obtained by adding carbon dioxide to the basic sulfurized alkaline earth metal alkyl phenate. The excess alkaline earth metal base can be added subsequent to the sulfurization step but is conveniently added at the same time as the alkaline earth metal base is added to neutralize the phenol.

Carbon dioxide and calcium hydroxide or oxide are the most commonly used materials to produce the basic or "overbased" phenates. A process wherein basic sulfurized alkaline earth metal alkylphenates are produced by adding carbon dioxide is shown in Hanneman, U.S. Pat. No. 3,178,368.

The Group II metal salts of dihydrocarbyl dithiophosphoric acids exhibit wear, antioxidant and thermal stability properties. Group II metal salts of phosphorodithioic acids have been described previously. See, for example, U.S. Pat. No. 3,390,080, columns 6 and 7, wherein these compounds and their preparation are described generally. Suitably, the Group II metal salts of the dihydrocarbyl dithiophosphoric acids useful in the lubricating oil composition of this invention contain from about 4 to about 12 carbon atoms in each of the hydrocarbyl radicals and may be the same or different and may be aromatic, alkyl or cycloalkyl. Preferred hydrocarbyl groups are alkyl groups containing from 4 to

8 carbon atoms and are represented by butyl, isobutyl, sec-butyl, hexyl, isohexyl, octyl, 2-ethylhexyl and the like. The metals suitable for forming these salts include barium, calcium, strontium, zinc and cadmium, of which zinc is preferred.

Preferably, the Group II metal salt of a dihydrocarbyl dithiophosphoric acid has the following formula:



wherein:

e. R_2 and R_3 each independently represent hydrocarbyl radicals as described immediately above, and
f. M_1 represents a Group II metal cation as described above.

The dithiophosphoric salt is present in the lubricating oil compositions of this invention in an amount effective to inhibit wear and oxidation of the lubricating oil. The amount ranges from about 0.1 to about 4 percent by weight of the total composition, preferably the salt is present in an amount ranging from about 0.2 to about 2.5 percent by weight of the total lubricating oil composition. The final lubricating oil composition will ordinarily contain 0.025 to 0.25% by weight phosphorus and preferably 0.05 to 0.15% by weight.

The finished lubricating oil may be single or multigrade. Multigrade lubricating oils are prepared by adding viscosity index (VI) improvers. Typical viscosity index improvers are polyalkyl methacrylates, ethylene-propylene copolymers, styrene-diene copolymers and the like. So-called decorated VI improvers having both viscosity index and dispersant properties are also suitable for use in the formulations of this invention.

The lubricating oil used in the compositions of this invention may be a mineral oil or a synthetic oil of lubricating viscosity, preferably suitable for use in the crankcase of an internal combustion engine. Crankcase lubricating oils ordinarily have a viscosity of about 1300 cSt at 0°F. (-18°C.) to 22.7 cSt at 210°F. (99°C.). The lubricating oils may be derived from synthetic or natural sources. Mineral oil for use as the base oil in this invention includes paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C_{6-12} alpha olefins such as 1-decene trimer, tetramer, and higher oligomers. Likewise, alkyl benzenes of proper viscosity, such as didodecyl benzene, can be used. Useful synthetic esters include the esters of both monocarboxylic acid and polycarboxylic acids as well as monohydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaproate, di-2-ethylhexyl adipate, dilaurylsebacate and the like. Complex esters prepared from mixtures of mono and dicarboxylic acid and mono and dihydroxy alkanols can also be used.

Blends of hydrocarbon oils with synthetic oils are also useful. For example, blends of 10 to 25 weight percent hydrogenated 1-decene trimer with 75 to 90 weight percent 33 cSt at 100°F. (38°C.) mineral oil gives an excellent lubricating oil base.

Other additives which may be present in the formulation include rust inhibitors, foam inhibitors, corrosion inhibitors, metal deactivators, pour point depressants, antioxidants, and a variety of other well-known additives.

The following examples are offered to specifically illustrate the invention. These examples and illustrations are not to be construed in any way as limiting the scope of the invention.

TESTING PROCEDURE

The candidate additives were tested for their compatibility in a bench test (PV3334) by suspending a fluorocarbon coupon (AK6) in an oil solution heated at 150°C for 96 hours (4 days) followed by measuring a change in the physical properties of the specimen, particularly the tensile strength (TS), and the percent elongation to break (EL) in accordance with DIN53504 procedure, and observing whether any cracks had developed at 120% elongation (CR). A passing test criteria included the following: no evidence of crack development; a tensile strength change of less than 20% (gain or loss); and an elongation change of less than 25% (gain or loss). Obviously, an ideal case would show no cracks and 0% change in TS and EL. This test procedure will be referred to above and later simply as the "VW Bench Test."

The baseline formulation used for testing a fluorocarbon coupon contained a dispersant (6% by weight), i.e., either a mono- or bis-succinimide; an overbased calcium hydrocarbyl sulfonate (30 mmol/kg); an overbased calcium phenate

(20 mmol/kg); mixed primary and secondary zinc dialkyl dithiophosphates (22.5 mmol/kg) ; and ethylene-propylene copolymer viscosity index improver (13% by weight) in 150N Exxon base oil. When borated additives were tested, these were added in appropriate percentages as top treats on top of the baseline formulation above.

FIRST SERIES OF RUNS

A series of experiments were run to determine the effect of substituents on borated catechols at one weight percent (1%) treat level using in some experiments a mono-succinimide and in other experiments a bis-succinimide. The succinimides were prepared as described above by the reaction of succinic anhydride with TEPA in the correct mole ratio to give either the desired mono- or bis-product. The results are summarized in Table 1 below.

Examples 15 to 19 do not form part of the claimed invention but assist in its understanding.

TABLE 1

Effect of Substitutions on Borated Catechols at 1.0 weight %

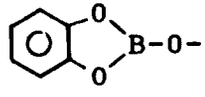
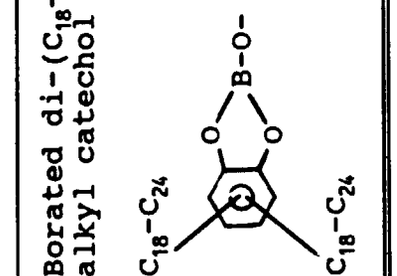
Example No.	Additive Compound	PPM BORON	C/B[5]	Succin-imide	TS[1]	EL[2]	CR[3]	PASS[4]
1	None	0	-	BIS	-39	-34	Yes	No
2	None	0	-	BIS	-31	-29	Yes	No
3	None	0	-	BIS	-32	-30	Yes	No
4	None	0	-	MONO	-52	-45	Yes	No
5	Catechol Borate 	620	3:2	BIS	+1	0	No	Yes
6	Same as 5	620	3:2	BIS	+3	-7	No	Yes
7	Same as 5	620	3:2	MONO	-21	-21	No	No
8	Same as 5	620	3:2	MONO	-12	-7	No	Yes
9	Same as 5	860	1:1	BIS	-8	+1	No	Yes
10	Same as 5	860	1:1	MONO	-12	-18	No	Yes
11	Same as 5	470	2:1	BIS	+6	-2	No	Yes
12	Same as 5	470	2:1	MONO	-16	-13	No	Yes

TABLE 1 (Continued)

13	Borated 4-t-butyl catechol	360	3:2	BIS	-14	-13	No	Yes
14	Same as 13	360	3:2	MONO	-47	-42	Yes	No
15	Borated C_{18}-C_{24} alkyl catechol	130	3:2	BIS	-21	-3	No	No
16	Same as 15	130	3:2	BIS	-22	-15	No	No
17	Same as 15	130	3:2	MONO	-57	-40	Yes	No
18	Borated 3,5-di-tertiary butyl catechol	320	3:2	BIS	-28	-27	No	No

TABLE 1 (Continued)

19	Borated di-(C_{18}-C_{24}) alkyl catechol 	110	3:2	MONO	-56	-50	No	No

1. TS = Change in Tensile Strength by DIN Test No. 53504. Change within ± 20 is needed to "Pass".
2. EL = Change in elongations by DIN Test No. 53504. Change within ± 25 is needed to "Pass".
3. CR = Cracks observed (DIN Test No. 53504). No observations of cracks is needed to "Pass".
4. PASS = Did the compositions pass the VW Bench Test.
5. C/B = Catechol to boron mole ratio.

Referring to Table 1, Examples 1-4 are base runs and show that the presence of mono- or bis-succinimides alone in the formulation without borated aromatic polyols, lack compatibility of the oil to the fluorocarbon elastomers, i.e., no

pass of the VW Bench Test.

The addition of 1% catechol borate (Ex. 5-12) to the bis-or mono-succinimide formulation results in a "Pass" of the VW Bench Test except for Example 7 which was a borderline pass, but which passed on repeating (Ex 8). It should be noted that the bis-compositions exhibited less change in tensile strength and elongation (Ex's 6, 9 and 11) than the mono- compositions (Ex's 7, 8, 10 and 12) since the mono-compositions contain more basic nitrogen and are more difficult to passivate as discussed above.

The use of borated t-butyl catechol results in passivation of the basic nitrogen (Ex 13) using bis-succinimides but fails using the mono-succinimides (Ex 14). Examples 27 and 28 in Table 2 below show that increasing the concentration of the borated t-butyl catechol to 2% results in a "PASS" with the mono-succinimide.

Examples 15-19 show that using only 1 weight percent of several different alkylated borated catechols within the scope of the invention is insufficient to passivate the fluorocarbon elastomers. Examples in Table 2 below show that increasing the concentrations of such catechols results in a PASS.

SECOND SERIES OF RUNS

A second series of experiments were run to determine the effect of concentration of the borated catechols on the bis-and mono-succinimides needed to obtain a Pass on the VW Bench Test. The various borated catechols were used in concentrations from 0.5 to 4 weight percent. The results are summarized in Table 2 below.

Examples 15, 17, 29 to 31, 19, and 32 to 35 do not form part of the claimed invention but assist in its understanding.

TABLE 2

Effect of Concentrations on Borated Catechols

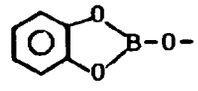
Example No.	Additive Compound	wt% Additive	PPM BORON	C/B[5]	Succinimide	TS[1]	EL[2]	CR[3]	PASS[4]
1	None	0	0	-	BIS	-39	-34	Yes	No
2	None	0	0	-	BIS	-31	-29	Yes	No
3	None	0	0	-	BIS	-32	-30	Yes	No
4	None	0	0	-	MONO	-52	-45	Yes	No
20	Catechol Borate 	0.5	310	3:2	BIS	-11	-15	No	Yes
21	Same as example 20	0.5	310	3:2	MONO	-51	-45	Yes	No
5	Same as example 20	1.0	620	3:2	BIS	+1	0	No	Yes
6	Same as example 20	1.0	620	3:2	BIS	+3	-7	No	Yes
7	Same as example 20	1.0	620	3:2	MONO	-21	-21	No	No
8	Same as example 20	1:0	620	3:2	MONO	-12	-7	No	Yes
22	Same as example 20	1.5	930	3:2	MONO	-5	0	No	Yes
23	Same as example 20	1.5	930	3:2	MONO	-5	-2	No	Yes
24	Same as example 20	2.0	1240	3:2	MONO	-8	+2	No	Yes

TABLE 2 (Continued)

25	Borated 4-t-butyl catechol	0.5	180	3:2	BIS	-15	-25	No	Yes
26	Same as example 25	0.5	180	3:2	MONO	-55	-51	Yes	No
13	Same as example 25	1.0	360	3:2	BIS	-14	-13	No	Yes
14	Same as example 25	1.0	360	3:2	MONO	-47	-42	Yes	No
27	Same as example 25	2.0	720	3:2	BIS	-6	-4	No	Yes
28	Same as example 25	2.0	720	3:2	MONO	-8	-4	No	Yes
15	Borated C_{18}-C_{24} alkyl catechol	1.0	130	3:2	BIS	-21	-3	No	No
17	Same as example 15	1.0	130	3:2	MONO	-57	-40	Yes	No
29	Same as example 15	2.0	260	3:2	BIS	-10	-10	No	Yes
30	Same as example 15	2.0	260	3:2	MONO	-44	-31	Yes	No
31	Same as example 15	4.0	520	3:2	MONO	-13	-17	No	Yes
19	Borated Di-(C_{18}-C_{24}) alkyl catechol	1.0	110	3:2	MONO	-56	-50	No	No
32	Same as example 19	2.0	220	3:2	BIS	-26	-30	No	No
33	Same as example 19	2.0	220	3:2	MONO	-54	-48	Yes	No

TABLE 2 (Continued)

34	Same as example 19	4.0	440	3:2	BIS	-16	-19	No	Yes
35	Same as example 19	4.0	440	3:2	MONO	-46	-38	Yes	No

1. TS = Change in Tensile Strength by DIN Test No. 53504. Change within ± 20 is needed to "Pass".
2. EL = Change in elongations by DIN Test No. 53504. Change within ± 25 is needed to "Pass".
3. CR = Cracks observed (DIN Test No. 53504). "Pass" means that no cracks were observed.
4. PASS = Did the compositions pass the VW Bench Test.
5. C/B = Catechol to boron mole ratio.

Referring to Table 2, it can be seen that increasing the concentration of the borated aromatic polyols of this invention

results in passivation of the fluorocarbon elastomers even with the higher alkylated catechols and in the presence of the higher basic nitrogen containing mono-succinimides (Ex 31). The use of even higher alkyl catechol [di (C_{18}-C_{24})] results in a Pass at the 4.0 wt. % level with the bis-succinimide (Ex 34).

Considering the data in Tables 1 and 2, and ignoring the effect of the alkyl group or the concentration of the additive, passing the VW Bench Test occurred with bis-succinimide dispersants at a minimum boron level of 180 ppm. With mono-succinimides, the minimum boron level required to pass the same VW Bench Test was 470 ppm B.

THIRD SERIES OF RUNS

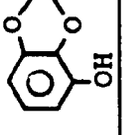
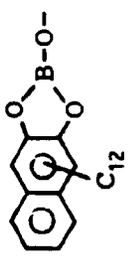
A third series of experiments were run to determine the effect of borate structure using a one weight percent (1 wt%) treat level of the additive in a lubricating oil formulation containing 6 weight percent of the bis-succinimide as the dispersant. The results are summarized in Table 3 below.

TABLE 3

Effect of Borate Structures

Example No.	Additive Compound	wt% Additive	PPM BORON	C/B[5]	TS[1]	EL[2]	CR[3]	PASS[4]
1	None	0	0	-	-39	-34	Yes	No
2	None	0	0	-	-31	-29	Yes	No
3	None	0	0	-	-32	-30	Yes	No
36	Borated Bissuccinimide	1.0	60	-	-32	-27	No	No
37	Triphenyl Borate	1.0	370	3:1	-28	-27	No	No
38	Triphenyl Borate	2.0	740	3:1	-39	-39	No	No
39	Glycerol Borate	1.0	740	3:2	-27	-30	No	No
40	Glycerol Borate	2.0	1480	3:2	------Not Soluble------			
41	Ethylene Glycol Borate	1.0	1070	3:2	-31	-32	No	No
42	Ethylene Glycol Borate	2.0	2140	3:2	------Not Soluble------			

TABLE 3 (Continued)

43	Glycerol Monooleate Borate	1.0	390	3:2	-33	-30	No	No
44	Glycerol Monooleate Borate	3.0	1170	3:2	-39	-36	No	No
45	2,5-di-tertiary Butyl Hydroquinone Borate	1.0	320	3:2	-41	-29	No	No
5	Catechol Borate	1.0	620	3:2	+1	0	No	Yes
46	Pyrogallol Borate 	1:0	540	3:2	-8	+1	No	Yes
47	Alkyl (C_{12})Naphthalene 2,3-diol Borate 	1.0	640	3:2	-4	+1	No	Yes

1. TS = Change in Tensile Strength by DIN Test No. 53504. Change within ± 20 is needed to "Pass".
2. EL = Change in elongations by DIN Test No. 53504. Change within ± 25 is needed to "Pass".
3. CR = Cracks observed (DIN Test No. 53504). No observations of cracks is needed to "Pass".
4. PASS = Did the compositions pass the VW Bench Test.
5. C/B = Catechol to boron or polyol to boron mole ratio.
6. In all Examples, the succinimide employed was bis-succinimide.

Referring to Table 3, the effect of using a borated aromatic polyol as defined in this invention is observed. For example, borating the bis-succinimide (Ex 36) is not successful, confirming the teachings of Anderson in Column 3, lines 3-5 of his U.S.P. 4,873,009 referred to above. Further, the boration and use of other hydroxy containing structures also fails as seen in Examples 37 through 45. Examples 5, 46 and 47 show that the aromatic polyol can be a single (Ex 5) or condensed ring (Ex 47) aromatic as long as two hydroxy groups are present on adjacent aromatic ring carbon

atoms (Compare Examples 5 and 46, which were successful, to Example 45 which was unsuccessful due to the hydroxy groups being on non-adjacent aromatic ring carbon atoms). The presence of an additional hydroxy group on the ring (pyrogallol) is acceptable (See Example 46).

FOURTH SERIES OF RUNS

A fourth series of experiments were run to determine the effect of various borating agents on the effectiveness of a C_{18}-C_{24} alkyl catechol for passivating the fluorocarbon polymer seals. The results are shown in Table 4 below.

TABLE 4

The Use of Various Borating Agents

Example No.[6]	Additive Compound	wt% Additive	PPM BORON	C/B[5]	TS[1]	EL[2]	CR[3]	PASS[4]	Borating Agent
1	None	0	0	-	-39	-34	Yes	No	---
2	None	0	0	-	-31	-29	Yes	No	---
3	None	0	0	-	-32	-30	Yes	No	---
48	Alkyl (C_{18}-C_{24}) Catechol-unborated	2.0	0	-	-37	-29	Yes	No	---
15	Borated (C_{18}-C_{24}) alkyl Catechol	1.0	130	3:2	-21	-3	No	No	Boric Acid ($B(OH)_3$)
29	Same as example 15	2.0	260	3:2	-10	-10	No	Yes	Boric Acid ($B(OH)_3$)
49	Alkyl Catechol Sodium Metaborate	1.0	140	-	-28	-22	No	No	$NaBO_2$
50	Alkyl Catechol Sodium Tetraborate	1.0	150	-	-38	-29	No	No	$Na_2B_4O_7$
51	Alkyl Catechol Lithium Metaborate	1.0	130	-	-25	-25	No	No	$LiBO_2$

1. TS = Change in Tensile Strength by DIN Test No. 53504. Change within ± 20 is needed to "Pass".
2. EL = Change in elongations by DIN Test No. 53504. Change within ± 25 is needed to "Pass".
3. CR = Cracks observed (DIN Test No. 53504). No observations of cracks is needed to "Pass".
4. PASS = Did the compositions pass the VW Bench Test.
5. C/B = Catechol to boron mole ratio.
6. In all Examples, the succinimide employed was the bis-succinimide.

Referring to Table 4, the use of boron salts, such as sodium or lithium borate, gives unsatisfactory results (Examples 49-51).

SEMISYNTHETIC AND SYNTHETIC BASE OILS

FIFTH SERIES OF RUNS

In the experiments summarized in Tables 1 through 4 above, only petroleum-derived, i.e., mineral base oils were used to screen the various additives for Viton® passivation. In a fifth series of experiments, extension was made to include semi-synthetic and fully synthetic base oil formulations. For example, in the case of semi-synthetic base oil, the following formulation was tested: bis-succinimide dispersant (5.8%), a mixture of low overbased and high overbased calcium sulfonates (3.7%), ZnDTP (1%), friction modifier (0.25%), and polyol ester (6%) in 150N BP base oil (22%), a synthetic polyalphaolefin (PAO) base oil (54%), and polyisoprene VI improver (7%), blended to a 5W40 specification. The PAO used was a mixture of decene-1 oligomers which was formulated from 4 and 6 cSt products obtained from Chevron Chemical Company. The borated additives were added as "top treats" on top of the reference formulation in the percentages given in the examples which are summarized in Table 5 below.

SYNTHETIC BASE OILS

The fully synthetic base oil was used in a formulation containing a mixture of dispersants (7.3%), an overbased calcium sulfonate (0.7%), highly overbased calcium phenate (3.4%), mixed zincs (2%), and polyol ester (8.3%) in a commercial synthetic PAO base fluid (as above) (68%) and polyisoprene VI improver (10.3%), blended to a 5W40 specification. As before, the borated additives were added as "top treats" on top of the reference formulation in the percentages given in the examples summarized in Table 5 below.

TABLE 5

Effect of Semisynthetic and Synthetic Base Stocks

Exam. No.	Additive Compound	wt% Additive	PPM BORON	C/B[5]	TS[1]	EL[2]	CR[3]	PASS[4]	Base Oil
52	None	---	---	---	-44	-38	Yes	No	54 wt% of a PAO #1[6]
53	None	---	---	---	-40	-39	Yes	No	54 wt% of a PAO #2[7]
54	None	---	---	---	-37	-34	No	No	100% of a PAO #3[8]
55	Borated alkyl (C_{18}-C_{24}) catechol	1.0	130	3:2	-25	-28	No	No	54% of a PAO #1
56	Same as example 55	2.0	260	3:2	-20	-17	No	Yes	54% of a PAO #1
57	Borated (C_{36}) alkyl catechol	1.0	120	3:2	-20	-31	No	No	54% of a PAO #2
58	Same as example 57	2.0	240	3:2	-24	-24	No	No	54% of a PAO #2
59	Same as example 57	2.5	300	3:2	-19	-20	No	Yes	100% of a PAO #3

TABLE 5 (Continued)

60	Borated catechol	1.0	560	3:2	-16	-10	No	Yes	100% of a PAO #3

1. TS = Change in Tensile Strength by DIN Test No. 53504. Change within ± 20 is needed to "Pass"
2. EL = Change in elongations by ASTM Test No. 53504. Change within ± 25 is needed to "Pass".
3. CR = Cracks observed (DIN Test No. 53504). No observations of cracks is needed to "Pass".
4. PASS = Did the compositions pass the VW Bench Test.
5. C/B = Catechol to boron mole ratio.
6. PAO #1 is a blend of 4 and 6 cSt products.
7. PAO #2 is similar to PAO #1, but of different batches.
8. PAO #3 is a blend of 6 and 8 cSt products.

Referring to Table 5, it can be seen that the semisynthetic and synthetic base oils are satisfactory for use in pre-

paring the compositions of this invention.

SIXTH SERIES OF RUNS

For reasons not fully understood, the most effective boron-containing compounds for passivation of the fluorocarbon elastomer, are also the borated compounds which showed considerable antioxidancy properties when examined in an oxidation bench test.

For example, when a fully formulated base oil reference was top treated with the given amount of additive, either in weight % or in ppm of boron for the boron-containing compounds, the results summarized in Table 6 below were obtained.

The reference oil formulation contained 3.5% dispersant, 50 mmol/kg calcium as hydrocarbyl sulfonates, 17 mmol/kg zinc dialkyl dithiophosphate, and 6.8% viscosity index improver in Chevron 100N base oil. The oxidation test employed herein measures the resistance of the test sample to oxidation using pure oxygen with a Dornte-type oxygen absorption apparatus [R. W. Dornte, "Oxidation of White Oils," Industrial and Engineering Chemistry, 28 p. 26 (1936)]. The conditions are: an atmosphere of pure oxygen exposed to the test oil, an oil temperature of 340° F. (171°C.) and an oxidation catalyst comprised of 0.69% Cu, 0.41% Fe, 8.0% Pb, 0.35% Mn, and 0.36% Sn (as naphthenates) in the oil [J. Amer. Soc. Lubr. Eng., Vol. 37, p. 722, (1981), Test 1H]. The time required for 100 g of the test sample to absorb 1.0 L. of oxygen is measured.

TABLE 6

Oxidation Bench Test Results

Example No.	Compound (WT%)	Boron, PPM in Oil Blend	Hrs to 1 L. Oxygen Uptake	Hrs Improvm. Over the Reference
61	Reference	0	10.6	---
62	Alkylcatechol (2)	0	11.0	-0.4
63	Borated Bissuccinimide	100	9.2	-1.4
64	Borated Bissuccinimide	213	7.7	-2.9
65	Borated Bissuccinimide	300	8.0	-2.6
		avg 201		avg -2.3
66	Borated Glycerol	100	8.0	-2.6
67	Monooleate	200	7.1	-3.5
68		300	7.0	-3.6
		avg 200		avg -3.2
69	Phenylborate	100	10.7	-0.1
70		200	10.2	-0.4
71		300	10.0	-0.6
		avg 200		avg -0.4
72	Alkylcatechols	136	15.2	+4.6
73	($R=C_{18}-C_{24}$) (Borated)	210	19.8	+9.2
74		315	25.4	+14.8
		avg 220		avg +9.5
75	Dialkylcatechols	100	10.9	+0.3
76	($R=C_{18}-C_{24}$) (Borated)	155	11.9	+1.3
77		229	13.4	+2.8
78		280	16.4	+5.8
		avg 191		avg +2.6

TABLE 6 (Continued)

79	Alkylcatechol (1) + Borated Glycerol Monooleate	100	14.6	+4.0	
80		200	12.9	+2.3	
81		300	12.9	+2.3	
		avg 200		avg +2.9	

Referring to Table 6, the addition of alkyl-catechol to a reference oil at 2%, practically had no anti-oxidancy effect (Example 62) as the data is typically reproducible to the extent of ± 0.5 hr. Addition of borated bis-succinimide (Examples 63-65), or borated glycerol monooleate (Examples 66-68), shows no antioxidancy, but actually prooxidant effect, indi-

cating that the reference oil was more stable in the absence of added borated compounds than in their presence. Addition of phenylborate (Examples 69-71) gave only a small prooxidant effect, but this value was not statistically different from the reference (Example 61) and for practical purposes was considered neutral. Borated alkylcatechol (Examples 72-74) (R=C_{18}-C_{24}) showed very positive antioxidant properties, and borated dialkylcatechols (Examples 75-78) (R=C_{18}-C_{24}) also showed antioxidant properties, but these were lower than those obtained in case of the monoalkylcatechols. Examples 79-81 show that when unborated alkylcatechol was added with borated glycerol monooleate, the addition of each individually led to either no effect or a small prooxidant effect previously, now showed a positive antioxidant effect.

SEVENTH SERIES OF RUNS

As was noted above, catechol borate and short chain alkyl catechol borates (1-8 carbons in the alkyl chain) were found to have unexpectedly superior dispersancy properties compared to long-chain alkyl catechol borates. The dispersancy properties are measured by the "dispersancy spot test" ("Test").

A general discussion of the Test can be found in A. Shilling's "Motor Oils and Engine Lubrications," Volume 1, Scientific Publications Limited, England, 1968, p. 2.53-2.84. One revision of the Test is set forth in Example 4 of U.S. Patent 4,199,462, Column 7, lines 13 et seq. The Test set forth in Example 4 of the '462 Patent has been modified for the seventh series of runs to be discussed below.

The working conditions of the seventh series of runs for the Test were as follows:

1 - Without water

5 g of artificial sludge containing approximately 2% of carbonaceous matter are added to 20 g of a reference SAE 30 oil plus a small amount of a catechol borate of this invention and mixed together, using a micro-crushing-mill (about 18,000 rpm): twice 30 seconds with a 15 second pause between the two.

The following conditions must be observed in each test:

- keep to the micro-crushing time
- keep to the interval between the two periods of micro-crushing
- use only 50 cc beakers

2 - With water

Same as above but add 1% water to the mixture. The oil to be tested is then examined by making spots:

- cold dispersion:
  Make a spot on the filter paper using a glass stirrer (diam 8 mm) dipped into the sample with or without water to about 2 cm taking the 3rd or the 4th drop.
- hot dispersion:
  Place 2 ccs of the sample to be tested in a test tube, place this in an acetophenone bath at 200°C for 1 or 10 minutes. A spot is then made, taking the first drop to fall from the glass stirrer.

6 spots are made in the following conditions:

1 room temperature without water
2 10 minutes at 200° without water
3 10 minutes at 250° without water
4 room temperature + water
5 1 minute at 200°C + water
6 10 minutes at 200°C + water

Important

- The spot at room temperature is made when the oil has cooled completely (approximately 15 minutes after micro-crushing). The micro-crushing raises the temperature of the oil to around 50 to 60°C).

The hot spots are made as soon as the tube is removed from the bath at 200°C.

- When applying the drop of oil to the filter paper never allow the glass stirrer to come into contact with the latter.

The results are obtained by measuring the spot after 48 hours of deposit on a flat surface protected from any contamination.

The "spot" consists of an inner darker circle of diameter "d" surrounded by a translucent area soaked with basic oil and forming a larger circle of diameter "D."

For each spot, the ratio d:D is calculated and multiplied by 100. The "best" dispersion would be where d:D equals 1 for each spot to give a combined maximum of 600 dispersion units.

When oils of similar dispersive properties are compared, it is possible simply to compare the total of the 6 spot ratios multiplied by 100.

The purpose of the seventh series of runs was to compare the dispersive properties of (1) catechol borate (2) butyl catechol borate and (3) a long-chain (average C_{22}) alkyl catechol borate with the reference SAE30 oil containing the sludge.

Catechol borate showed a gain of about 50 units over the reference value of 396. t-Butyl catechol borate showed a gain of about 18 units while the long chain alkyl catechol borate showed a loss of about 25 units. The attached Figure is a plot of these data with the carbon number of the alkyl group on the x-axis and a loss or gain in dispersancy on the y-axis. The Figure suggests that alkylcatechol borates with alkyl groups below 10 carbon i.e., 8 or 9, should not only provide passing results in the VW Bench Test, but also offer no loss in the overall dispersancy, a quite unexpected result.

While catechol borate has the advantages set forth above, it and the lower alkyl catechol borates have low solubility in base oils. For example, catechol borate was soluble only to the extent of about 0.3 weight percent or less.

The following Table 7 demonstrates that alkyl catechol borates containing a long chain alkyl group can effectively be employed to enhance the solubility of the less soluble catechol borate in the base oil.

The following chart demonstrates the fact that alkyl-catechol borates containing a long alkyl group can effectively be employed to enhance the solubility of the less soluble catechol borate in the formulated base oil. For example, catechol borate was soluble only to the extent of about <0.3%, but this value was exceeded by adding an alkylcatechol containing a long (avg C22) alkyl group.

TABLE 7

SOLUBILITY OF CATECHOL BORATE IN VITON® BASELINE OIL*					
CATECHOL BORATE, 5.6% B (CB) ALKYL (C_{18} - C_{24}) BORATE, 1.2% B (ACB)					
Ratio CB/ACB	1/1	1/2	1/3	1/4	1/0
Wt% (CB + ACB) in baseline oil	2	2	2	2	1
Wt% CB in baseline oil	1	0.67	0.5	0.4	1
ppm in final oil blend	680	530	430	420	560
Appearance	hazy little solids	very slight haze, no solids	clear bright, no solids	clear bright, no solids	hazy some solids

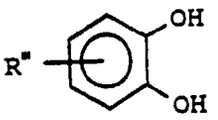
* at room temperature (20°C)

The invention is not to be limited to the examples but only to the claims set forth below.

Claims

1. The use of a borated aromatic polyol, in a lubricating composition containing a minor proportion of a basic nitrogen compound, for the purpose of improving the compatibility of said lubricating oil towards fluorocarbon polymer engine

seals, said borated aromatic polyol being obtainable by borating an aromatic polyol having the formula:



where R''' is selected from the group consisting of H; OH; or an alkyl group having from 1 to 8 carbon atoms.

2. A use according to claim 1, wherein the basic nitrogen compound is a succinimide.

3. A use according to claim 2 wherein the succinimide comprises the reaction product of a C_8-C_{500} polybutene succinimic acid or anhydride compound and an alkylene polyamine.

4. A use according to claim 3 wherein the amount of the borated aromatic polyol is at least the stoichiometric amount to the basic nitrogen present in the composition.

5. A use according to claim 4 wherein the borated aromatic polyol is borated catechol.

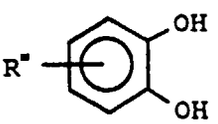
6. A use according to claim 4 wherein the borated aromatic polyol is borated pyrogallol.

7. A use according to claim 4 wherein the borated aromatic polyol is borated tertiary butyl catechol.

8. A use according to claim 4 wherein the weight percent of said succinimide is from 1 to 20 weight percent of said composition.

9. A use according to claim 1 which further contains a sufficient amount of a long-chain alkyl borated catechol wherein the alkyl group has at least 10 carbon atoms to aid in solubilizing said borated aromatic polyol.

10. A lubricant composition comprising a major proportion of a lubricating oil; a minor proportion of at least one basic nitrogen compound and a minor but effective compatibilizing amount of a borated aromatic polyol as an additive to passavate fluorocarbon polymer seals, said aromatic polyol being obtainable by borating an aromatic polyol having the formula:



wherein R''' is selected from the group consisting of H; OH; or an alkyl group having from 1 to 8 carbon atoms.

11. A composition according to claim 10 wherein the basic nitrogen compound is a succinimide.

12. A composition according to claim 11 wherein the succinimide comprises the reaction product of a C_8-C_{500} polybutene succinimic acid or anhydride compound and an alkylene polyamine.

13. A composition according to claim 12 wherein the amount of the borated aromatic polyol is at least the stoichiometric amount to the basic nitrogen present in the composition.

14. A composition according to claim 13 wherein the borated aromatic polyol is borated catechol.

15. A composition according to claim 13 wherein the borated aromatic polyol is borated pyrogallol.

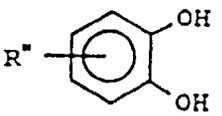
16. A composition according to claim 13 wherein the borated aromatic polyol is borated tertiary butyl catechol.

17. A composition according to claim 13 wherein the weight percent of said succinimide is from 1 to 20 weight percent of said composition.

18. A composition according to claim 10 which further contains a sufficient amount of a long-chain alkyl borated catechol wherein the alkyl group has at least 10 carbon atoms to aid in solubilizing said borated aromatic polyol.

Patentansprüche

1. Verwendung eines borierten aromatischen Polyols in einer Schmiermittelzusammensetzung, welche zu einem geringen Anteil eine basische Stickstoffverbindung enthält, mit dem Zweck, die Kompatibilität des Schmieröls zu Motorendichtungen aus Fluorkohlenstoffpolymer zu verbessern, wobei das borierte aromatische Polyol erhältlich ist durch Borieren eines aromatischen Polyols der Formel:



worin R''' ausgewählt ist aus der Gruppe mit H, OH oder einer Alkylgruppe mit 1-8 Kohlenstoffatomen.

2. Verwendung nach Anspruch 1, wobei die basische Stickstoff-Verbindung ein Succinimid ist.

3. Verwendung nach Anspruch 2, wobei das Succinimid das Reaktionsprodukt enthält aus einer C_8-C_{500}-Polybuten-Bernsteinsäure- oder -anhydridverbindung und einem Alkylenpolyamin.

4. Verwendung nach Anspruch 3, wobei das borierte aromatische Polyol zumindest in stöchiometrischer Menge zu dem basischen Stickstoff in der Zusammensetzung vorliegt.

5. Verwendung nach Anspruch 4, wobei das borierte aromatische Polyol boriertes Catechol ist.

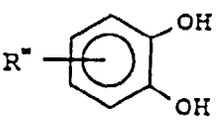
6. Verwendung nach Anspruch 4, wobei das borierte aromatische Polyol boriertes Pyrogallol ist.

7. Verwendung nach Anspruch 4, wobei das borierte aromatische Polyol boriertes tert.-Butylcatechol ist.

8. Verwendung nach Anspruch 4, wobei das Succinimid in 1 bis 20 Gew.% der Zusammensetzung vorliegt.

9. Verwendung nach Anspruch 1, die zudem eine ausreichende Menge eines borierten Catechols mit langkettigem Alkyl vorsieht, wobei die Alkylgruppe mindestens 10 Kohlenstoffatome hat, so dass die Solubilisierung des borierten aromatischen Polyols unterstützt wird.

10. Schmiermittelzusammensetzung, umfassend eine größere Menge eines Schmieröls, eine geringere Menge mindestens einer basischen Stickstoffverbindung und eine geringere, jedoch wirksam kompatibel machende Menge eines borierten aromatischen Polyols als Additiv zur Passivierung der Fluorkohlenstoffpolymerdichtungen, wobei das aromatische Polyol erhältlich ist durch Borieren eines aromatischen Polyols der Formel:



worin R''' ausgewählt ist aus der Gruppe mit H, OH oder einer Alkylgruppe mit 1-8 Kohlenstoffatomen.

11. Zusammensetzung nach Anspruch 10, wobei die basische Stickstoffverbindung ein Succinimid ist.

12. Zusammensetzung nach Anspruch 11, wobei das Succinimid das Reaktionsprodukt enthält aus einer C_8-C_{500}-Polybuten-Bernsteinsäure- oder -anhydridverbindung und einem Alkylenpolyamin.

13. Zusammensetzung nach Anspruch 12, wobei das borierte aromatische Polyol mindestens in stöchiometrischer Menge zu dem basischen Stickstoff in der Zusammensetzung vorliegt.

14. Zusammensetzung nach Anspruch 13, wobei das borierte aromatische Polyol boriertes Catechol ist.

15. Zusammensetzung nach Anspruch 13, wobei das borierte aromatische Polyol boriertes Pyrogallol ist.

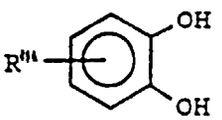
16. Zusammensetzung nach Anspruch 13, wobei das borierte aromatische Polyol boriertes tert.-Butylcatechol ist.

17. Zusammensetzung nach Anspruch 13, wobei das Succinimid in 1 bis 20 Gew.% der Zusammensetzung vorliegt.

18. Zusammensetzung nach Anspruch 10, die zudem eine ausreichende Menge an boriertem Langkettenalkyl-Catechol enthält, wobei die Alkylgruppe mindestens 10 Kohlenstoffatome hat, so dass die Solubilisierung des borierten aromatischen Polyols unterstützt wird.

Revendications

1. Utilisation d'un polyol aromatique boraté dans une composition lubrifiante contenant une moindre proportion d'un composé contenant de l'azote basique, en vue d'améliorer la compatibilité de cette huile lubrifiante vis-à-vis de joints en polymère fluorocarboné de moteurs, ce polyol aromatique boraté pouvant être obtenu par boratation d'un polyol aromatique répondant à la formule :



dans laquelle R"' est choisi dans le groupe consistant en H ; OH ; ou un groupe alkyle ayant 1 à 8 atomes de carbone.

2. Utilisation suivant la revendication 1, dans laquelle le composé contenant de l'azote basique est un succinimide.

3. Utilisation suivant la revendication 2, dans laquelle le succinimide comprend le produit de réaction d'un acide ou anhydride succinimique à substituant polybutène en C_8 à C_{500} et d'une alkylènepolyamine.

4. Utilisation suivant la revendication 3, dans laquelle la quantité de polyol aromatique boraté est au moins égale à la quantité stoechiométrique relative à l'azote basique présent dans la composition.

5. Utilisation suivant la revendication 4, dans laquelle le polyol aromatique boraté est le catéchol boraté.

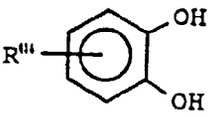
6. Utilisation suivant la revendication 4, dans laquelle le polyol aromatique boraté est le pyrogallol boraté.

7. Utilisation suivant la revendication 4, dans laquelle le polyol aromatique boraté est le tertio-butyl-catéchol boraté.

8. Utilisation suivant la revendication 4, dans laquelle le pourcentage en poids du succinimide va de 1 à 20 % en poids de la composition.

9. Utilisation suivant la revendication 1, comprenant en outre une quantité suffisante d'un catéchol boraté à groupe alkyle à longue chaîne, dont le groupe alkyle a au moins 10 atomes de carbone, pour faciliter la solubilisation de ce polyol aromatique boraté.

10. Composition lubrifiante comprenant une proportion dominante d'une huile lubrifiante ; une proportion moindre d'au moins un composé contenant de l'azote basique et une quantité compatibilisante moindre mais efficace d'un polyol aromatique boraté comme additif pour passiver des joints en polymère fluorocarboné, ce polyol aromatique pouvant être obtenu par boratation d'un polyol aromatique répondant à la formule :



dans laquelle R''' est choisi dans le groupe consistant en H ; OH ; ou un groupe alkyle ayant 1 à 8 atomes de carbone.

11. Composition suivant la revendication 10, dans laquelle le composé contenant de l'azote basique est un succinimide.

12. Composition suivant la revendication 11, dans laquelle le succinimide comprend le produit de réaction d'un acide ou anhydride succinimique à substituant polybutène en C_8 à C_{500} et d'une alkylènepolyamine.

13. Composition suivant la revendication 12, dans laquelle la quantité de polyol aromatique boraté est au moins la quantité stoechiométrique relative à l'azote basique présente dans la composition.

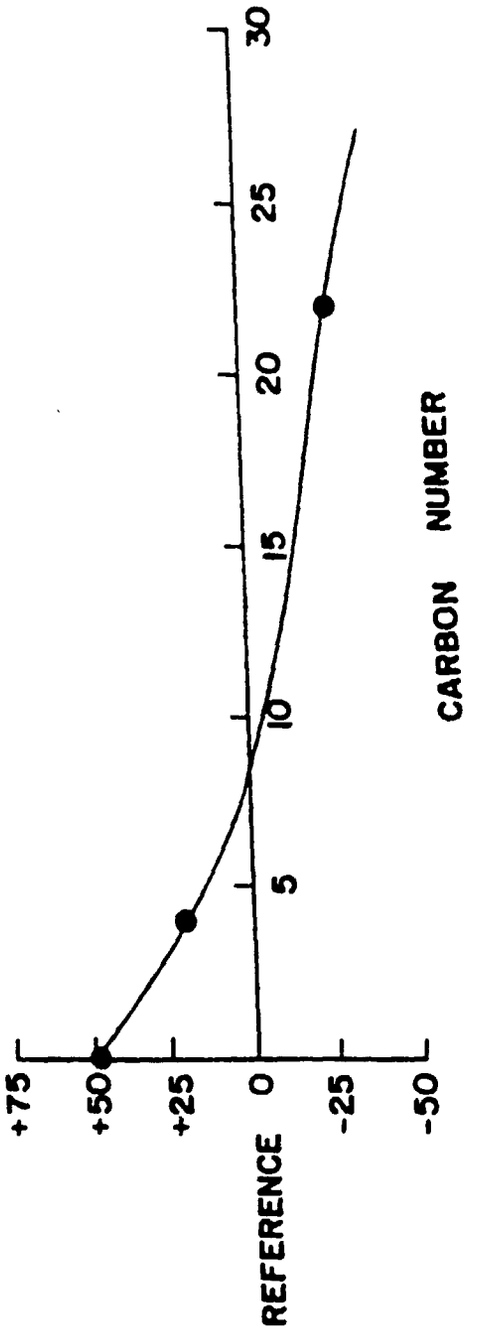
14. Composition suivant la revendication 13, dans laquelle le polyol aromatique boraté est le catéchol boraté.

15. Composition suivant la revendication 13, dans laquelle le polyol aromatique boraté est le pyrogallol boraté.

16. Composition suivant la revendication 13, dans laquelle le polyol aromatique boraté est le tertio-butyl-catéchol boraté.

17. Composition suivant la revendication 13, dans laquelle le pourcentage en poids du succinimide va de 1 à 20 % en poids de la composition.

18. Composition suivant la revendication 10, qui contient en outre une quantité suffisante d'un catéchol boraté portant un groupe alkyle à longue chaîne, dont le groupe alkyle a au moins 10 atomes de carbone, pour faciliter la solubilisation de ce polyol aromatique boraté.


30
25
20
15
10
5
CARBON NUMBER
+75
+50
+25
0
-25
-50
REFERENCE