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MODIFIED DISPERSANT COMPOSITIONS

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(56) Prior Art Documents
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(57) Claim

1. An oil soluble dispersant composition formed by reacting a basic nitrogen-containing ashless dispersant (i) with at least one dibasic acylating agent containing up to 12 carbon atoms per molecule and (ii) with at least one boron compound, said reactions (i) and (ii) being conducted concurrently or sequentially in any order such that the ashless dispersant is chemically modified via acylation in (i) and by boronation in (ii).

6. A process which comprises reacting a basic nitrogen-containing ashless dispersant with at least one dibasic acylating agent having up to 12 carbon atoms in the molecular and with at least one boron compound, such reactions being conducted concurrently or sequentially in any order such that the ashless dispersant is chemically modified via acylation and boronation.

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PATENTS ACT 1990
COMPLETE SPECIFICATION

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INVENTION TITLE:

Modified dispersant compositions

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

This invention relates to novel modified ashless dispersants, to processes for their production, and to their use in liquid hydrocarbonaceous media. As used herein, the term "ashless" is used in the normal art-recognized sense of denoting that the composition is devoid of metals other than boron, such as alkali or alkaline earth metals, zinc or other metals that tend to produce metal-containing residues.

A continuing problem in the art of lubrication is to provide lubricant compositions which satisfy the demands imposed upon them by the original equipment manufacturers. One such requirement is that the lubricant not contribute to premature deterioration of seals, clutch face plates or other parts made from fluoroelastomers. Unfortunately, and as is well known, basic nitrogen-containing dispersants such as succinimide dispersants commonly used in oils tend to exhibit a strong adverse effect upon fluoroelastomers, by causing them to lose their flexibility and tensile strength, to become embrittled, and in severe cases, to disintegrate. Contemporary test methods for evaluating fluoroelastomer compatibility of lubricants and functional fluids are the Volkswagen P.VW 3334 Elastomer Compatibility Test, the CCMC Oil-Elastomer Seal Test (CEC L-39-T-87), and the fluoroelastomer seal test in accordance with the TO-3 Caterpillar Specification.

Methods of post-treating various nitrogen-containing dispersants with various substances are well documented in the literature, e.g., in U.S. Patents 3,087,936; 3,184,411; 3,185,645; 3,185,704; 3,200,107; 3,254,025; 3,256,185; 3,278,550; 3,280,034; 3,281,428; 3,282,955; 3,284,410; 3,312,619; 3,338,832; 3,344,069; 3,366,569; 3,367,943; 3,369,021; 3,373,111; 3,390,086; 3,458,530; 3,470,098; 3,502,677; 3,511,780; 3,513,093; 3,541,012; 3,551,466; 3,558,743; 3,573,205; 3,652,616; 3,718,663; 3,749,695; 3,865,740; 3,865,813; 3,954,639; 4,338,205; 4,401,581; 4,410,437; 4,428,849; 4,548,724; 4,554,086; 4,608,185; 4,612,132; 4,614,603; 4,615,826; 4,645,515; 4,686,054; 4,710,201; 4,713,191; 4,746,446; 4,747,850; 4,747,963; 4,747,964; 4,747,965; and 4,857,214 and British Patents 1,085,903 and 1,162,436.

In accordance with this invention, there is provided an oil soluble dispersant

composition formed by reacting a basic nitrogen-containing ashless dispersant (i) with at least one dibasic acylating agent containing up to 12, preferably up to 8, more preferably up to 6, and most preferably 4, carbon atoms, and (ii) with at least one boron compound, said reactions (i) and (ii) being conducted concurrently or sequentially in any order such that the initial ashless dispersant is chemically modified via acylation in (i) and by boronation in (ii). Whilst any boron compound or compounds can be used provided it is or they are capable of reacting with the basic nitrogen-containing ashless dispersant to introduce boron moieties into the dispersant, it is preferred to conduct the boronation in (ii) using at least one boron acid or ester or anhydride thereof, or any combination thereof.

The preferred acylating agents used in the reaction identified as (i) above are maleic anhydride, maleic acid, fumaric acid, malic acid or any combination of any two, any three or all four of these compounds.

Ashless dispersants utilised in the foregoing processing include hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acids, Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines, and amine dispersants formed by reacting high molecular weight aliphatic or alicyclic halides with amines, such as polyalkylene polyamines. Mixtures of such dispersants can also be used.

Such basic nitrogen-containing ashless dispersants are well-known lubricating oil additives, and methods for their preparation are extensively described in the patent literature, e.g., in U. S. Patents 3,018,247; 3,018,250; 3,018,291; 3,172,892; 3,185,704; 3,219,666; 3,272,746; 3,275,554; 3,361,673; 3,368,972; 3,413,347; 3,438,757; 3,454,555; 3,539,633; 3,565,804; 3,576,743; 3,697,574; 3,725,277; 3,725,480; 3,726,882; 3,798,247; 3,803,039; and 4,234,435.

The preferred ashless dispersants are hydrocarbyl succinimides in which the hydrocarbyl substituent is a hydrogenated or unhydrogenated polyolefin group, preferably a polyisobutene group having a number average molecular weight (as measured by gel permeation chromatography) of 250-10,000, more preferably 500-5,000, and most preferably 750-2,500. The ashless dispersant is most preferably an aikenyl succinimide such as is available commercially from Ethyl Petroleum

Additives, Inc. and Ethyl Petroleum Additives, Ltd. as HITEC® 644 and HITEC® 646 additives.

Other embodiments of this invention are (A) the provision of a dispersant prepared as above having the ability when formulated in a finished engine lubricating oil of satisfying the requirements of the ASTM sequence VE engine tests for API "SG" performance (see ASTM 315 H, part III Seq. VE), and the requirements of the Volkswagen P.VW 3334 Elastomer Compatibility Test and/or the requirements of the CCMC Oil-Elastomer Compatibility Test (CEC L-39-T-87) and/or the fluoro-elastomer seal test in accordance with the TO-3 Caterpillar Specification, (B) the provision of lubricating oil additive concentrates containing an effective amount of an improved dispersant composition of this invention, and (C) an oil of lubricating viscosity containing an effective amount of an improved dispersant composition of this invention.

Still further embodiments of this invention are processes for producing the improved dispersant compositions of this invention by reacting a basic nitrogen-containing ashless dispersant with at least one dibasic acylating agent containing up to 12, preferably up to 8, more preferably up to 6, and most preferably 4, carbon atoms, and with at least one boron compound, said reactions being conducted concurrently or sequentially in any order such that the initial ashless dispersant is chemically modified via acylation and by boronation.

These and other embodiments and features of this invention will be apparent from the ensuing description and appended claims.

Basic Nitrogen-Containing Ashless Dispersants

As noted above, the process of this invention can be applied to any basic nitrogen-containing ashless dispersant susceptible to acylation and boronation. Thus the process can be applied to any of the basic nitrogen-containing dispersants referred to hereinabove.

The preferred basic nitrogen-containing dispersants utilised in the practise of this invention are the hydrocarbyl succinimides. As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between a hydrocarbyl substituted succinic acylating agent and a polyamine and is intended

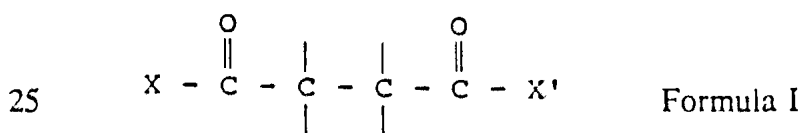
to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

Of the succinimides, most preferred are those formed by use as one of the reactants of at least one aliphatic hydrocarbyl substituted succinic acylating agent in which the hydrocarbyl substituent contains an average of at least 40 carbon atoms. A preferred category of such acylating agents is comprised of at least one hydrocarbyl substituted succinic acylating agent in which the substituent is principally alkyl, alkenyl, or polyethylenically unsaturated alkenyl, or any combination thereof and wherein such substituent has an average of 50-5,000 carbon atoms. Particularly preferred for use as the acylating agent is (a) at least one polyisobutenyl substituted succinic acid, (b) at least one polyisobutenyl substituted succinic anhydride, or (c) a combination of (a) at least one polyisobutenyl substituted succinic acid and (b) at least one polyisobutenyl substituted succinic anhydride, the polyisobutenyl substituent being derived from polyisobutene having a number average molecular weight in the range of 700-5,000.

As is well known, the substituted succinic acylating agents are those which can be characterized by the presence within their structure of two groups or moieties, i.e.:

(1) a substituent group derived from a polyalkene which is characterized by an $\overline{M}_n$ (number average molecular weight) value of 500-10,000, preferably 700-5000, and

(2) a succinic group characterized by the structure



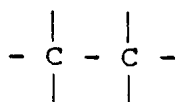
wherein X and X' are the same or different provided at least one of X and X' is such that the substituted succinic acylating agent can function as a carboxylic acylating agent, i.e., esterify alcohols, form amides or amine salts with ammonia or amines, form metal salts with reactive metals or basically reacting metal compounds, and otherwise function as a conventional carboxylic acid acylating agent.

Transesterification and transamidation reactions are considered, for purposes of this invention, as conventional acylation reactions.

Thus, X and/or X' is usually -OH, -O-hydrocarbyl; -O·M⁺ where M⁺ represents one equivalent of a metal, ammonium or amine cation, -NH₂, -Cl, or -Br, or X and X' together can be -O- so as to form the anhydride. The specific identity of any X or X' group which is not one of the above is not critical so long as its presence does not prevent the remaining group from entering into acylation reactions.

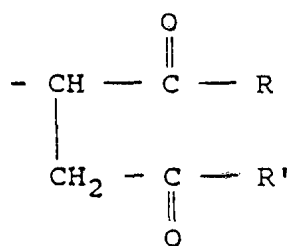
Preferably, however, X and X' are each such that both carboxyl functions of the succinic group can enter into acylation reactions.

One of the unsatisfied valences in the grouping



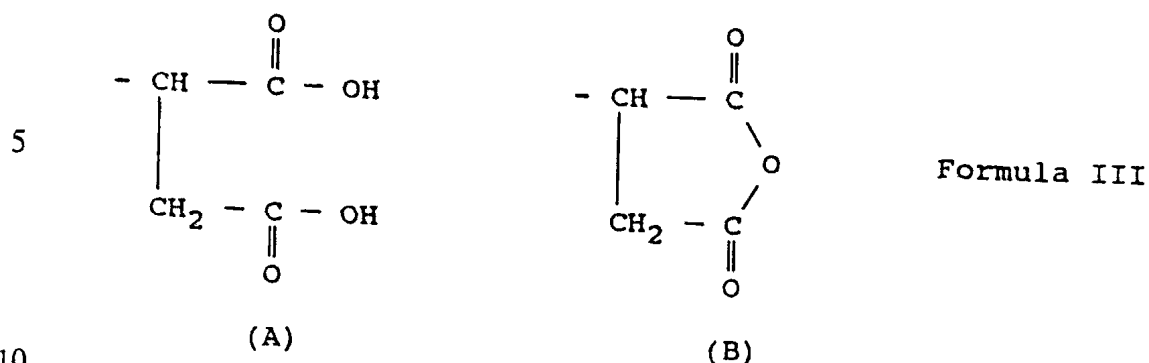
of Formula I forms a carbon-to-carbon bond with a carbon atom in the substituent group. While other such unsatisfied valence may be satisfied by a similar bond with the same or different substituent group, all but the said one such valence is usually satisfied by a hydrogen atom.

The succinic groups of the succinic acylating agents will normally correspond to the formula



Formula II

wherein R and R' are each independently selected from the group consisting of -OH, -Cl, -OR" (R" = lower alkyl), and when taken together, R and R' are -O-. In the latter case the succinic group is a succinic anhydride group. All the succinic groups in a particular succinic acylating agent need not be the same, but they can be the same. Preferably, the succinic groups will correspond to Formula III(A) or Formula III(B)



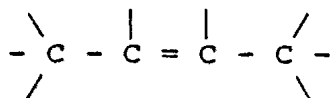
or mixtures of III(A) and III(B). Production of substituted succinic acylating agents wherein the succinic groups are the same or different is within ordinary skill of the art and can be accomplished through conventional procedures such as treating the substituted succinic acylating agents themselves (for example, hydrolysing the anhydride to the free acid or converting the free acid to an acid chloride with thionyl chloride) and/or selecting the appropriate maleic or fumaric reactants.

The polyalkenes from which the substituent groups are derived are homopolymers and interpolymers of polymerisable olefin monomers of 2-16 carbon atoms; usually 2-6 carbon atoms. The interpolymers are those in which two or more olefin monomers are interpolymers according to well-known conventional procedures to form polyalkenes having units within their structure derived from each of said two or more olefin monomers. Thus, the polymers used include binary copolymers, terpolymers, tetrapolymers, and the like. The polyalkenes from which the substituent groups are derived are often referred to as polyolefin(s).

The olefin monomers from which the polyalkenes are derived are polymerisable olefin monomers characterised by the presence of one or more ethylenically unsaturated groups (i.e., $>\text{C}=\text{C}<$); that is, they are mono-olefinic monomers such as ethylene, propylene, 1-butene, isobutene, and 1-octene or polyolefinic monomers (usually diolefinic monomers) such as 1,3-butadiene and isoprene.

These olefin monomers are usually polymerisable terminal olefins; that is, olefins characterised by the presence in their structure of the group $>\text{C}=\text{CH}_2$. However, polymerisable internal olefin monomers characterised by the presence within

their structure of the group



5 can also be used to form the polyalkenes. When internal olefin monomers are employed, they normally will be employed with terminal olefins to produce polyalkenes which are interpolymers. When a particular polymerisable olefin monomer can be classified as both a terminal olefin and an internal olefin, it is usually categorised as a terminal olefin. An example of such a monomer is 1,3-pen-
10 tadiene (i.e., piperylene).

While the polyalkenes from which the substituent groups of the succinic acylating agents are derived generally are hydrocarbon polyalkenes, they can contain non-hydrocarbon groups such as lower alkoxy, lower alkyl mercapto, hydroxy, mercapto, oxo, nitro, halo, cyano, carboalkoxy (i.e., -C(O)-O-alkyl, where "alkyl" is usually lower alkyl, namely an alkyl group containing up to about 7 carbon atoms), alkanoyloxy (or carbalkoxy, i.e., alkyl-C(O)-O-, where "alkyl" is usually lower alkyl), and the like, provided the non-hydrocarbon substituents do not substantially interfere with formation of the substituted succinic acid acylating agents. When present, such non-hydrocarbon groups normally will not contribute more than about 10% by weight of the total weight of the polyalkenes. Since the polyalkene can contain such non-hydrocarbon substituents, it is apparent that the olefin monomers from which the polyalkenes are made can also contain such substituents. Normally, however, as a matter of practicality and expense, the olefin monomers and the polyalkenes used are free from non-hydrocarbon groups, except chloro groups which usually facilitate the formation of the substituted succinic acylating agents.

Although the polyalkenes may include aromatic groups (especially phenyl groups and lower alkyl- and/or lower alkoxy-substituted phenyl groups such as p-tert-butylphenyl) and cycloaliphatic groups such as would be obtained from polymerisable cyclic olefins or cycloaliphatic substituted-polymerisable acyclic olefins, the polyalkenes usually will be free from such groups. Nevertheless, polyalkenes derived from interpolymers of both 1,3-dienes and styrenes such as 1,3-butadiene and styrene or 4-tert-butyl-styrene are exceptions to this generalisation. Similarly, the

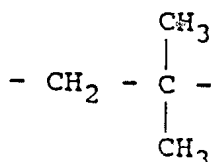
olefin monomers from which the polyalkenes are prepared can contain both aromatic and cycloaliphatic groups.

Generally speaking aliphatic hydrocarbon polyalkenes free from aromatic and cycloaliphatic groups are preferred for use in preparing the substituted succinic acylating agents. Particularly preferred are polyalkenes which are derived from homopolymers and interpolymers of terminal hydrocarbon olefins of 2-8 carbon atoms, most especially from 2-4 carbon atoms. While interpolymers of terminal olefins are usually preferred, interpolymers optionally containing up to about 40% of polymer units derived from internal olefins of up to about 8 carbon atoms are also preferred. The most preferred polyalkenes are polypropylenes and polyisobutenes.

Specific examples of terminal and internal olefin monomers which can be used to prepare the polyalkenes according to conventional, well-known polymerisation techniques include ethylene; propylene; 1-butene; 2-butene; isobutene; 1-pentene; 1-hexene; 1-heptene, 1-octene; 1-nonene; 1-decene; 4-methyl-1-pentene; propylenetetramer; diisobutylene; isobutylene trimer; 1,2-butadiene; 1,3-butadiene; 1,2-pentadiene; 1,3-pentadiene; 1,4-pentadiene; isoprene; 1,5-hexadiene; 2-chloro-1,3-butadiene; 2-methyl-1-heptene; 4-cyclohexyl-1-butene; 3-pentene; 4-octene; 3,3-dimethyl-1-pentene; styrene; 2,4-dichlorostyrene; divinylbenzene; vinyl acetate; allyl alcohol; 1-methyl-vinyl acetate; acrylonitrile; ethyl acrylate; methyl methacrylate; ethyl vinyl ether; and methyl vinyl ketone. Of these, the hydrocarbon polymerisable monomers are preferred and of these hydrocarbon monomers, the terminal olefin monomers are particularly preferred.

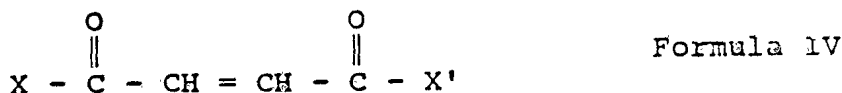
Specific examples of polyalkenes include polypropylenes; polybutenes; ethylene-propylene, styrene-isobutene, isobutene-1,3-butadiene, propene-isoprene, isobutene-chloroprene, isobutene-4-methylstyrene, 1-hexene-1,3-hexadiene, 1-octene-1-hexene, 1-heptene-1-pentene, 3-methyl-1-butene-1-octene, and 3,3-dimethyl-1-pentene-1-hexene copolymers; and terpolymers of isobutene, styrene and piperylene. More specific examples of such interpolymers include copolymer of 95% (by weight) of isobutene with 5% (by weight) of styrene; terpolymer of 98% of isobutene with 1% of piperylene and 1% of chloroprene; terpolymer of 95% of isobutene with 2% of 1-butene and 3% of 1-hexene; terpolymer of 60% of isobutene

with 20% of 1-pentene and 20% of 1-octene; copolymer of 80% of 1-hexene and 20% of 1-heptene; terpolymer of 90% of isobutene with 2% of cyclohexene and 8% of propylene; and copolymer of 80% of ethylene and 20% of propylene. Preferred sources of polyalkenes are the polyisobutenes obtained by polymerisation of C₄ refinery streams which contain both n-butene and isobutene in various proportions using a Lewis acid catalyst such as aluminum trichloride or boron trifluoride. These polybutenes usually contain predominantly (for example, greater than about 80% of the total repeating units) of repeating units of the configuration

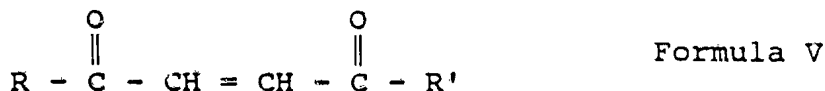


In preparing polyalkenes, conventional techniques known to those skilled in the art include suitably controlling polymerisation temperatures, regulating the amount and type of polymerisation initiator and/or catalyst, employing chain terminating groups in the polymerisation procedure, and the like. Other conventional techniques such as stripping (including vacuum stripping) a very light end and/or oxidatively or mechanically degrading high molecular weight polyalkene to produce lower molecular weight polyalkenes can also be used.

In preparing the substituted succinic acylating agents, one or more of the above-described polyalkenes is reacted with one or more maleic or fumaric acidic reactants of the general formula



wherein X and X' are as defined hereinbefore. Preferably the maleic and fumaric reactants will be one or more compounds corresponding to the formula



wherein R and R' are as previously defined herein. Ordinarily the maleic or fumaric reactants will be maleic acid, fumaric acid, maleic anhydride, or a mixture of two or

more of these. The maleic reactants are usually preferred over the fumaric reactants because the former are more readily available and are, in general, more readily reacted with the polyalkenes (or derivatives thereof) to prepare the substituted succinic acylating agents. The most preferred reactants are maleic acid, maleic anhydride, and mixtures of these.

Any of a variety of known procedures can be used to produce the substituted succinic acylating agents. For convenience and brevity, when the term "maleic reactant" is used hereafter, the term is generic to the reactants corresponding to Formulas IV and V above including mixtures of such reactants.

One procedure for preparing the substituted succinic acylating agents is illustrated, in part, by the two-step procedure described in U.S. Patent 3,219,666. It involves first chlorinating the polyalkene until there is an average of at least about one chloro group for each molecule of polyalkene. Chlorination involves merely contacting the polyalkene with chlorine gas generally at a temperature of 75°C-125°C until the desired amount of chlorine is incorporated into the chlorinated polyalkene. If desired, a diluent can be used in the chlorination procedure. Suitable diluents for this purpose include poly- and perchlorinated and/or fluorinated alkanes and benzenes.

The second step in the two-step chlorination procedure is to react the chlorinated polyalkene with the maleic reactant, usually in a mole ratio of about 1:1, at a temperature usually within the range of 100°C-200°C -- a mole of chlorinated polyalkene being regardable as the weight of chlorinated polyalkene corresponding to the $\bar{M}_n$ value of the unchlorinated polyalkene. However, a stoichiometric excess of maleic reactant can be used, for example, a mole ratio of 1:2. If an average of more than about one chloro group per molecule of polyalkene is introduced during the chlorination step, then more than one mole of maleic reactant can react per molecule of chlorinated polyalkene. Accordingly, the ratio of chlorinated polyalkene to maleic reactant may be referred to in terms of equivalents, an equivalent weight of chlorinated polyalkene being the weight corresponding to the $\bar{M}_n$ value divided by the average number of chloro groups per molecule of chlorinated polyalkene. The equivalent weight of a maleic reactant is its molecular weight. Thus, the ratio of

chlorinated polyalkene to maleic reactant will normally be such as to provide about 1-2 equivalents of maleic reactant for each mole of chlorinated polyalkene with the understanding that it is normally desirable to provide an excess of maleic reactant; for example, an excess of about 5% to about 25% by weight. Unreacted excess
5 maleic reactant may be stripped from the reaction product, usually under vacuum, or reacted during a further stage of the process as explained below.

The resulting polyalkenyl-substituted succinic acylating agent is, optionally, again chlorinated if the desired number of succinic groups are not present in the product. If there is present, at the time of this subsequent chlorination, any excess
10 maleic reactant from the second step, the excess will react as additional chlorine is introduced during the subsequent chlorination. Otherwise, additional maleic reactant is introduced during and/or subsequent to the additional chlorination step. This technique can be repeated until the total number of succinic groups per equivalent weight of substituent groups reaches the desired level.

Another procedure for preparing substituted succinic acid acylating agents
15 utilises a process described in U.S. Patent 3,912,764 and U.K. Patent 1,440,219. According to that process, the polyalkene and the maleic reactant are first reacted by heating them together in a direct alkylation procedure. When the direct alkylation step is completed, chlorine is introduced into the reaction mixture to
20 promote reaction of the remaining unreacted maleic reactants. According to the patents, 0.3 to 2 or more moles of maleic anhydride are used in the reaction for each mole of olefin polymer; i.e., polyalkene. The direct alkylation step is conducted at temperatures of 180°C to 250°C. During the chlorine-introducing stage, a temperature of 160°C to 225°C is employed.

Other known processes for preparing the substituted succinic acylating
25 agents include the one-step process described in U.S. Patents 3,215,707 and 3,231,587. Basically, this process involves preparing a mixture of the polyalkene and the maleic reactant in suitable proportions and introducing chlorine into the mixture, usually by passing chlorine gas through the mixture with agitation, while maintaining a
30 temperature of at least about 140°C.

Usually, where the polyalkene is sufficiently fluid at 140°C and above,

there is no need to utilise an additional substantially inert, normally liquid solvent/diluent in the one-step process. However, if a solvent/diluent is employed, it is preferably one that resists chlorination such as the poly- and per-chlorinated and/or -fluorinated alkanes, cycloalkanes, and benzenes.

5 Chlorine may be introduced continuously or intermittently during the one-step process. The rate of introduction of the chlorine is not critical although, for maximum utilisation of the chlorine, the rate should be about the same as the rate of consumption of chlorine in the course of the reaction. When the introduction rate of chlorine exceeds the rate of consumption, chlorine is evolved from the reaction
10 mixture. It is often advantageous to use a closed system, including superatmospheric pressure, in order to prevent loss of chlorine so as to maximize chlorine utilisation.

The minimum temperature at which the reaction in the one-step process takes place at a reasonable rate is about 140°C. Thus, the minimum temperature at which the process is normally carried out is in the neighborhood of 140°C. The
15 preferred temperature range is usually 160°C-220°C. Higher temperatures such as 250°C or even higher may be used but usually with little advantage. In fact, excessively high temperatures may be disadvantageous because of the possibility that thermal degradation of either or both of the reactants may occur at excessively high temperatures.

20 In the one-step process, the molar ratio of maleic reactant to chlorine is such that there is at least about one mole of chlorine for each mole of maleic reactant to be incorporated into the product. Moreover, for practical reasons, a slight excess, usually in the neighborhood of about 5% to about 30% by weight of chlorine, is utilised in order to offset any loss of chlorine from the reaction mixture. Larger
25 amounts of excess chlorine may be used.

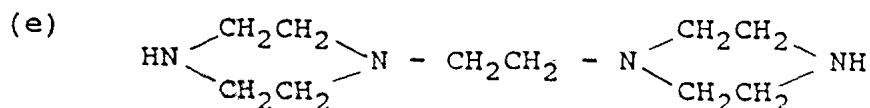
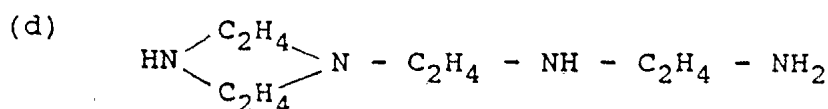
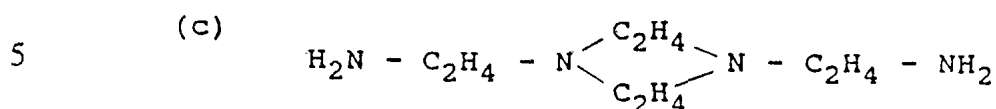
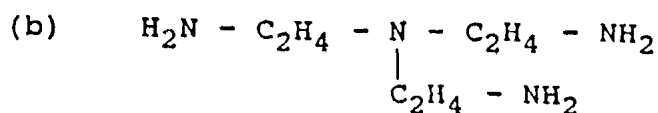
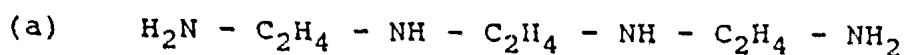
Further details concerning procedures for producing the substituted acylating agents have been extensively described in the patent literature, such as for example in U.S. Patent 4,234,435. Thus, further amplification of such procedures herein is deemed unnecessary.

30 The other principal reactant utilised in forming the succinimides which preferably are used in the process of this invention is one or a mixture of polyamines

which preferably has at least one primary amino group in the molecule and which additionally contains an average of at least two other amino nitrogen atoms in the molecule. For best results, the polyamines should contain at least two primary amino groups in the molecule.

5 One preferred type of polyamines is comprised of alkylene polyamines such as those represented by the formula $H_2N(CH_2)_n(NH(CH_2)_m)_mNH_2$ wherein n is 2-10 (preferably 2-4, more preferably 2-3, and most preferably 2) and m is 0-10, (preferably 1-6). Illustrative are ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, spermine, pentaethylenhexamine, 10 propylenediamine (1,3-propanediamine), butylenediamine (1,4-butanediamine), hexamethylenediamine (1,6-hexanediamine), decamethylenediamine (1,10-decanediamine), and the like. Preferred for use is tetraethylenepentamine or a mixture of ethylenepolyamines which approximates tetraethylenepentamine. Commercially available mixtures of polyethylenepolyamines (e.g., E-100 and S-1107 15 available from Dow Chemical Company) often contain minor amounts of cyclic species such as aminoalkyl-substituted piperazines and the like.

Another preferred type of polyamines is comprised of hydrocarbyl polyamines containing 10-50 weight percent acyclic alkylene polyamines and 50-90 weight percent cyclic alkylene polyamines. Preferably such mixture is a mixture 20 consisting essentially of polyethylene polyamines, especially a mixture having an overall average composition approximating that of polyethylene pentamine or a mixture having an overall average composition approximating that of polyethylene tetramine. Another useful mixture has an overall average composition approximating that of polyethylene hexamine. In this connection, the terms "polyalkylene" and "polyethylene", when utilised in conjunction with such terms as "polyamine", 25 "tetramine", "pentamine", "hexamine", etc., denote that some of the adjacent nitrogen atoms in the product mixture are joined by a single alkylene group whereas other adjacent nitrogen atoms in the product mixture are joined by two alkylene groups thereby forming a cyclic configuration, i.e., a substituted piperaziny structure. For 30 example, the following mixture of compounds:



is termed herein a "polyethylene tetramine" inasmuch as its overall composition is that of a tetramine (four amino groups per molecule) in which acyclic components (a) and (b) have three ethylene groups per molecule, cyclic components (c) and (d) have four ethylene groups per molecule, and cyclic component (e) has five ethylene groups per molecule. Thus, if the above mixture contains 10-50 weight percent of components (a) and (b) -- or either of them -- and from 90-50 weight percent of components (c), (d) or (e) -- or any two or all three of them -- it is a polyethylene tetramine suitable for use in the practise of this invention. Small amounts of lower and/or higher molecular weight species may of course be present in the mixture.

Among the especially preferred embodiments of this invention are formation of a succinimide product by:

1) use of a mixture of polyalkylene polyamines (10-50% acyclic; 90-50% cyclic) having an overall composition approximating that of polyalkylene pentamine and further characterised by containing on a weight basis:

- a) 2-10% of polyalkylene tetramines;
- b) 60-85% of polyalkylene pentamines;
- c) 10-20% of polyalkylene hexamines; and
- d) up to 10% lower and/or higher analogs of the foregoing.

2) use of a mixture of polyalkylene polyamines (10-50% acyclic; 90-50% cyclic) having an overall composition approximating that of

polyalkylene pentamine and further characterised by containing on a weight basis:

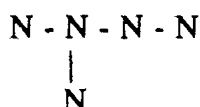
- a) at least 30% of the cyclic isomer depicted as



- b) at least 10% of the cyclic isomer depicted as



- c) at least 2% of the acyclic branched isomer depicted as



and

- d) at least 5% of the acyclic linear isomer depicted as

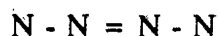


3) use of a mixture of polyalkylene polyamines (10-50% acyclic; 90-50% cyclic) having an overall composition approximating that of polyalkylene tetramine and further characterised by containing on a weight basis:

- a) at least 5% linear acyclic alkylene polyamines;
b) at least 10% branched acyclic alkylene polyamines; and
c) at least 60% cyclic alkylene polyamines.

4) use of a mixture of polyalkylene polyamines (10-50% acyclic; 90-50% cyclic) having an overall composition approximating that of polyalkylene tetramine and further characterised by containing on a weight basis:

- a) at least 30% of the cyclic isomer depicted as



- b) at least 20% of the cyclic isomer depicted as

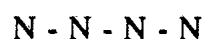


- c) at least 10% of the acyclic branched isomer depicted as



and

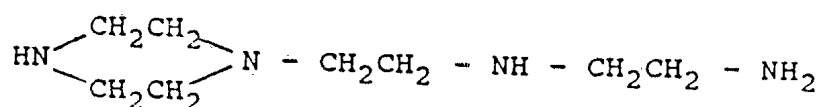
- d) at least 5% of the acyclic linear isomer depicted as



In the structural representations depicted in 2) and 4) above, the " - " (whether horizontal or vertical) represents an alkylene group each of which contains up to 6 carbon atoms, preferably 2-4 carbon atoms, and most preferably is the ethylene

(dimethylene) group, i.e., the $-\text{CH}_2\text{CH}_2-$ group. Similarly, the " = " represents a pair of such alkylene groups each having up to 6 carbon atoms and preferably having from 2-4 carbon atoms each. In the most preferred cases, the " = " represents a pair of ethylene (dimethylene) groups, each having the formula $-\text{CH}_2\text{CH}_2-$. As is indicated by the structural representations presented above, both of the alkylene groups in the cyclic structure depicted as " = " extend between the same pair of proximate nitrogen atoms.

In the above depictions, hydrogen atoms satisfying the trivalent character of the nitrogen atoms are not shown. Thus, when " - " is ethylene and " = " is a pair of ethylene groups, the depiction "N = N - N - N" is a simplified version of the formula:



Also suitable are aliphatic polyamines containing one or more ether oxygen atoms and/or one or more hydroxyl groups in the molecule. Mixtures of various polyamines of the type referred to above are also suitable.

In principle, therefore, any polyamine having at least one primary amino group and an average of at least three amino nitrogen atoms in the molecule can be used in forming the succinimide utilised in the practise of this invention. Product mixtures known in the trade as "triethylenetetramine", "tetraethylenepentamine", and "pentaethylenehexamine" are most preferred.

In forming the initial preferred succinimide used in the practise of this invention mole ratios of the hydrocarbyl substituted succinic acylating agent to polyamine reactant ranges from 1 : 1 to 4 : 1, and preferably from 1.5 : 1 to 3 : 1.

Dibasic Acylating Agent

A wide variety of dibasic acylating agents can be reacted with the basic nitrogen-containing ashless dispersant (e.g., succinimide, Mannich reaction product, succinic acid ester-amide, etc.) in the reaction of (i) above. The principal requirement is that such acylating agent contain at most 12 carbon atoms in the molecule, preferably up to 8 carbon atoms in the molecule, and more preferably up to 6 carbon atoms in the molecule. The most preferred acylating agents for use in reaction (i) contain 4 carbon atoms in the molecule. Thus use can be made of

dibasic acids and anhydrides, esters and acyl halides thereof which contain a total of up to 12 carbon atoms in the molecule (excluding carbon atoms of an esterifying alcohol). Among such compounds are azelaic acid, adipic acid, succinic acid, lower alkyl-substituted succinic acid, succinic anhydride, lower alkyl-substituted succinic anhydride, glutaric acid, pimelic acid, suberic acid, sebacic acid, and like dibasic acids, anhydrides, acyl halides, and esters which contain (excluding carbon atoms of esterifying alcohols) up to 12 carbon atoms in the molecule. Preferred are maleic acid, maleic anhydride, fumaric acid and malic acid. Most preferred is maleic anhydride.

Boron Compounds

The other reactant(s) with which the basic nitrogen-containing dispersant is reacted either before, during or subsequent to reaction with the above dibasic acylating agent is a boron compound or mixture of boron compounds capable of introducing boron-containing species into the ashless dispersant undergoing such reaction. Any boron compound, organic or inorganic, capable of undergoing such reaction can thus be used. Accordingly, use can be made of such inorganic boron compounds as the boron acids, and the boron oxides, including their hydrates. Typical organic boron compounds include esters of boron acids, such as the orthoborate esters, metaborate esters, biborate esters, pyroboric acid esters, and the like. Thus, use can be made of such compounds as, for example, boron acids such as boric acid, boronic acid, tetraboric acid, metaboric acid, pyroboric acid, esters of such acids, such as mono-, di- and tri-organic esters with alcohols having 1-20 carbon atoms, e.g., methanol, ethanol, propanol, isopropanol, the butanols, the pentanols, the hexanols, the octanols, the decanols, ethylene glycol, propylene glycol and the like, and boron oxides such as boron oxide and boron oxide hydrate. The preferred boron reactant is boric acid, sometimes referred to as orthoboric acid. Also suitable are alkyl boranes, alkyl boroxines, diborane and diborane-amine addition complexes, and many other reactive boron compounds.

Reaction Conditions

In conducting the foregoing reactions, any temperature at which the desired reaction(s) occur at a satisfactory reaction rate can be used. Ordinarily, the acylation reaction between the basic nitrogen-containing dispersant (boronated or unboronated) and the dibasic acylating agent is conducted at temperatures in the range of 80-200°C, more preferably 140-180°C. The boronation reaction is likewise

normally performed at temperatures within either of the foregoing ranges. However, departures from these ranges can be made whenever deemed necessary or desirable. These reactions may be conducted in the presence or absence of an ancillary diluent or liquid reaction medium, such as a mineral lubricating oil solvent. If the reaction is conducted in the absence of an ancillary solvent of this type, such is usually added to the reaction product on completion of the reaction. In this way the final product is in the form of a convenient solution in lubricating oil and thus is compatible with a lubricating oil base stock. Suitable solvent oils include lubricating oils having a viscosity (ASTM D 445) of 2-40, preferably 3-12 centistokes (cSt) at 100°C, with the primarily paraffinic mineral oils such as Solvent 100 Neutral being particularly preferred. Other types of lubricating oil base stocks can be used, such as synthetic lubricants including polyesters, poly- α -olefins, and the like. Blends of mineral oil and synthetic lubricating oils are also suitable for various applications in accordance with this invention.

The proportions of the reactants will to some extent be dependent on the nature of the basic-nitrogen containing dispersant being utilised, principally the content of basic nitrogen therein. Thus optimal proportions may, in some cases, be best defined by performing a few pilot experiments. Generally speaking, however, the dibasic acylating agent is employed in amounts ranging from 0.01 to 0.5 moles per average equivalent of nitrogen in the initial ashless dispersant(s), with the proviso that the resultant product contains at least 0.05 equivalent of basic nitrogen. Preferably the amount of dibasic acylating agent employed ranges from 0.02 to 0.3 mole per average equivalent of nitrogen in the initial ashless dispersant with the proviso that the resultant product contains at least 0.1 equivalent of basic nitrogen. In the case of use of a succinimide as the initial ashless dispersant, it is preferred to utilise an amount of the dibasic acylating agent such that the total mole ratio of (a) dibasic acylating agent plus (b) the aliphatic hydrocarbyl substituted succinic acylating agent used in forming the initial succinimide falls in the range of 1.5-3.5 moles of (a) and (b) per mole of polyamine, more preferably 1.6-2.8 moles of (a) and (b) per mole of polyamine, and most preferably 1.6-2.2 moles of (a) and (b) per mole of polyamine. Here again, departures from such proportions may be utilised if found efficacious in any given situation.

In the case of the boron reactant, the amounts used should be sufficient to introduce up to about 5%, and preferably 0.05-2.5% of boron (expressed as weight

% of elemental boron) into the overall final co-reacted dispersant.

It will be understood of course that in any given case the amount of dibasic acylating agent and boron compound used should be sufficient to provide a product having both satisfactory fluoroelastomer compatibility and adequate dispersancy performance.

Modified Processing

As noted above, the dispersants of this invention are formed by subjecting a basic nitrogen-containing ashless dispersant to two reactions, namely, acylation with at least one dibasic acylating agent and boronation with at least one boronation reagent. Ordinarily these reactions will be conducted either concurrently or in sequence. It is, of course, not necessary that both reactions be conducted in the same plant or at periods of time proximate to each other. For example, in one embodiment of this invention, boronated basic nitrogen-containing ashless dispersants which are available as articles of commerce need only be subjected to acylation with a dibasic acylating agent of the type described hereinabove in order to produce a novel boronated-acylated ashless dispersant of this invention. Likewise, one may procure a suitable acylated basic nitrogen-containing ashless dispersant from a given supplier (i.e., a basic nitrogen-containing ashless dispersant which has been subjected to acylation with a dibasic acylating agent of the type described hereinabove) and subject the same to boronation in order to produce a novel acylated-boronated ashless dispersant of this invention. In short, the novel products of this invention can be produced in accordance with this invention by two or more distinct and separate parties, if desired.

Further Treatments

Although ordinarily unnecessary, the acylated, boronated ashless dispersants of this invention can be reacted with one or more additional treating agents before, during or after either or both of the above-referred-to acylating and boronation reactions. Treating agents used for this purpose include, for example, carbon disulphide, hydrogen sulphide, sulphur, sulphur chloride, alkenyl cyanides, mono-, tri-, and tetra- carboxylic acid acylating agents, aldehyde, ketones, urea, thiourea, guanidine, dicyanodiamide, hydrocarbyl phosphates, hydrocarbyl phosphites, hydrocarbyl thiophosphates, hydrocarbyl thiophosphites, phosphorus sulphides, phosphorus oxides, phosphoric acid, phosphorous acid, hydrocarbyl thiocyanates, hydrocarbyl isocyanates, hydrocarbyl isothiocyanates, epoxides, episulphides,

formaldehyde or formaldehyde producing compounds plus phenols, sulphur plus phenols, and many others.

Since treating processes involving numerous treating reagents are known as regards treatment of various ashless dispersants, further details concerning such technology are readily available in the literature, e.g., the patents listed in the third paragraph of this specification.

Utilities

The novel compositions of this invention can be used as ashless dispersants in a wide variety of oleaginous fluids and as detergents or deposit reducers in hydrocarbonaceous fuels such as gasoline, diesel fuel, kerosene, burner fuel, gas oil, jet fuel, turbine fuel, and the like. They can be used in lubricating oil and functional fluid compositions, such as automotive crankcase lubricating oils, automatic transmission fluids, gear oils, hydraulic oils, cutting oils, etc. The lubricant may be a mineral oil, a synthetic oil, a natural oil such as a vegetable oil, or a mixture thereof, e.g., a mixture of a mineral oil and a synthetic oil. Suitable mineral oils include those of appropriate viscosity refined from crude oil of any source including Gulf Coast, Midcontinent, Pennsylvania, California, Alaska, Middle East, North Sea and the like. Standard refinery operations may be used in processing the mineral oil.

Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid α -olefin polymers of appropriate viscosity. Especially useful are hydrogenated or unhydrogenated liquid oligomers of C_6 - C_{16} α -olefins, such as hydrogenated or unhydrogenated α -decene trimer. Alkyl benzenes of appropriate viscosity, e.g., didodecylbenzene, can also be used.

Useful synthetic esters include the esters of monocarboxylic and polycarboxylic acids with monohydroxy alcohols and polyols. Typical examples are didodecyl adipate, trimethylolpropane tripelargonate, pentaerythritol tetracaproate, di-(2-ethylhexyl) adipate, and dilauryl sebacate. Complex esters made from mixtures of mono- and di-carboxylic acids and mono- and/or polyhydric alkanols can also be used.

Typical natural oils that may be used include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and the like. Such oils may be partially or fully hydrogenated, if desired.

Viscosity index improvers may be included in the mineral, synthetic and

natural oils (or any blends thereof) in order to achieve the viscosity properties deemed necessary or desirable.

5 The finished lubricating oil compositions and additive concentrates of this invention containing the present ashless dispersant systems will usually also contain other well-known additives in order to partake of their special properties. Among the numerous additives which can be employed in the lubricants and functional fluids and additive concentrates of this invention are those of the types described hereinafter.

10 The lubricants and functional fluids of this invention are of particular utility in applications wherein the oil of lubricating viscosity comes in contact with fluoro-elastomers. In such applications, the compatibility of the lubricant or functional fluid of this invention so utilised, is significantly enhanced as compared to the corresponding lubricant or functional fluid containing the corresponding untreated basic nitrogen-containing ashless dispersant.

15 The concentrations of the ashless dispersants of this invention in oleaginous fluids will generally fall in the range of up to about 10 weight percent, for example 1-9 weight percent. When used in fuel compositions, amounts of up to about 5 weight percent are typical.

20 The following examples, in which all parts and percentages are by weight, illustrate, but do not limit, and should not be construed as limiting, the practise of this invention.

EXAMPLE 1

25 In a first stage reaction, polyisobutenylsuccinic anhydride (PIBSA) formed from polyisobutylene (number average molecular weight = 1300) and tetraethylene pentamine (TEPA) in a mole ratio of 1.8:1 are reacted at 165-170°C for 4 hours. In a second stage reaction, maleic anhydride (MA) is added to the first stage reaction product in amount equivalent to 0.35 mole per mole of TEPA used in the first stage and the resultant mixture is heated at 165-170°C for 1.5 hours after which oil is added. In a third stage reaction, boric acid is added to the second stage reaction mixture at a temperature of 150-155°C in an amount corresponding to 4.0 moles per 30 mole of TEPA initially employed. The mixture is heated at 150°C for one hour and then water formed in the third stage reaction is removed by applying a vacuum of 40 mm for one hour. The resulting succinimide is both acylated and boronated and had a nitrogen content of 1.74%, and a boron content of 1.20%.

EXAMPLE 2

The procedure of Example 1 is repeated except that the amount of boric acid is reduced to 3.0 moles per mole of TEPA initially used. The final product, diluted to 1.70% nitrogen content with 100 solvent neutral mineral oil contains 0.82% boron.

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EXAMPLE 3

Repetition of Example 1 wherein the amount of boric acid is still further reduced to 2.0 moles per mole of TEPA initially used yields a concentrate (diluted as in Example 1) having a boron content of 0.62%.

EXAMPLE 4

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Example 1 is repeated but using 3.0 moles of boric acid per mole of TEPA initially used. The product concentrate (diluted as in Example 1) contains 0.88% boron.

EXAMPLE 5

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The procedure of Example 1 is repeated except that the reaction with boric acid is conducted before the reaction with maleic anhydride and the amount of boric acid used corresponds to 3.0 moles per mole of TEPA used in the first stage reaction. The final product (diluted as in Example 1) contains 0.9% boron.

EXAMPLE 6

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Example 5 is repeated except that the maleic anhydride and the boric acid are concurrently reacted with the succinimide formed in the first stage reaction. One such product on dilution with 100 solvent neutral mineral oil contained 1.66% nitrogen and 0.87% boron.

EXAMPLE 7

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In the first stage reaction, polyisobutenylsuccinic anhydride (PIBSA) formed from polyisobutylene (number average molecular weight = 1300) and tetraethylene pentamine (TEPA) in a mole ratio of 1.8:1 are reacted at 165-170°C for 4 hours and then mineral oil added. In a second stage reaction, maleic anhydride (MA) is added to the first stage reaction product in an amount equivalent to 0.3 moles per mole of TEPA used in the first stage and the resultant mixture is heated at 165-170°C for 1 1/2 hours. In a third stage reaction, boric acid (BA) is added to the second stage reaction product in an amount equivalent to 3.0 moles per mole of TEPA used in the first stage and the resultant mixture is heated at 150-155°C for 2 1/2 hours. The additive concentrate has a nitrogen content of 1.8% and a boron content of 0.90%.

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EXAMPLE 8

The procedure of Example 7 is repeated except that in the first stage the PIBSA and TEPA are reacted in a molar ratio of 1.7:1. In the second stage the MA is used in amount equivalent to a mole ratio of 0.4:1 relative to the TEPA used in the first stage. In the third stage, the boric acid (3.0 moles per mole of TEPA used in the first stage reaction) is added in an oil slurry. The product on dilution has a nitrogen content of 1.95% and a boron content of 0.64%.

EXAMPLE 9

In the first stage reaction, polyisobutenylsuccinic anhydride (PIBSA) (number average molecular weight = 1200 and TEPA are reacted in a mole ratio of 1.8:1. In a second stage, maleic anhydride is added to the first stage reaction product in an amount equivalent to 0.35 mole per mole of TEPA used in the first stage and the resultant mixture is heated at 165-170°C for 1 1/2 hours after which mineral oil is added. In a third stage reaction, boric acid is added to the second stage reaction product in an amount equivalent to 0.4 mole per mole of TEPA used in the first stage and the resultant mixture is heated at 150-155°C for 3 hours. The product has a nitrogen content of 1.85% and a boron content of 0.15%.

In order to determine the compatibility of various succinimide dispersants with fluoroelastomers, a series of finished crankcase lubricating oils for use in internal combustion engines containing various substituted succinimide dispersants were formulated. Each such oil contained, in addition to the succinimide dispersant, conventional amounts of overbased sulphonates, zinc dialkyl dithiophosphate, antioxidant, viscosity index improver, rust inhibitor, and antifoam agent to provide an SAE 15W/40 crankcase lubricant oil. The respective lubricants containing the succinimide dispersants of Examples 1-6 and 9 each contained an amount of such dispersant to provide a nitrogen content of 0.10%. In the case of the lubricants containing the succinimide dispersants of Examples 7 and 8, the nitrogen contents provided by the dispersants were 0.13%.

The resultant finished lubricating oils were subjected to the Volkswagen P.VW 3334 Elastomer Compatibility Test. The results are summarized in Table 1.

Table 1 - Results of Fluoroelastomer Seal Tests

	<u>Succinimide Used</u>	<u>Change in Elongation to Break Compared to Fresh Seal, %</u>	<u>Tensile Strength Compared to Fresh Seal, %</u>	<u>Cracking Observed</u>
5	Example 1	-17	-18	None
	Example 2	-11	-16	None
	Example 3	-27	-33	None
10	Example 4	-15	-12	None
	Example 5	-18	-13	None
	Example 6	-12	- 7	None
	Example 7	-12	-13	None
	Example 8	-30	-35	None
15	Example 9	-37	-41	None

In contrast, a corresponding untreated succinimide gives results in the above test in the order of -45% elongation change, -58% tensile strength change and it exhibits cracking.

Another feature of this invention is that the combined acylating and boronation reactions, whether run serially in either order or concurrently, can yield products having lower viscosities and consequent improved handleability as compared to corresponding products formed using either acylation or boronation only. For example a succinimide formed as in the first stage of Example 1 and boronated with boric acid to a level of 1.6% boron (1.8% nitrogen) has a viscosity of approximately 2900 cSt at 100°C. A product formed by reacting PIBSA with TEPA and thereafter reacting the succinimide with maleic anhydride (MA) (mole ratios of PIBSA : TEPA : MA = 2.05 : 1 : 1. (1.8% nitrogen) has a viscosity of 4500 cSt at 100°C. But a product of this invention formed from PIBSA, TEPA and MA (mole ratio: 1.8 : 1 : 0.3 respectively) and a boron content of 0.9% (1.8% nitrogen) has a viscosity at 100°C of approximately 1500 cSt.

The effectiveness of the products of this invention was demonstrated in a series of engine tests. For this purpose, a finished crankcase

lubricating oil was formulated to contain 7% by weight of a succinimide dispersant concentrate produced as in Example 2, in addition to conventional amounts of overbased sulphonates, zinc dialkyl dithiophosphate, antioxidant, viscosity index improver, rust inhibitor, and antifoam agent to provide an SAE 15W-40 lubricating oil. This lubricant was subjected to the ASTM Sequence VE Engine Test procedure wherein the results summarised in Table 2 were obtained.

Table 2 - Results of Sequence VE Test

	<u>Determination</u>	<u>Rating</u>	<u>Pass/Fail Value</u>
10	Rocker Arm Cover Sludge	8.2	7.0 Min.
	Average Sludge	9.2	9.0 Min.
	Piston Skirt Varnish	6.9	6.5 Min.
	Average Varnish	5.5	5.0 Min.
	Average Wear (mils)	2.65	5.00 Max.
15	Maximum Wear (mils)	3.30	15.00 Max

A formulation similar to that used in the above Sequence VE Test was subjected to the M102E Test (CEC L-41-T-88 Test Procedure). In this case the SAE 15W-40 lubricating oil contained 5.8% by weight of the ashless dispersant of this invention produced as in Example 4. It was found that an average sludge value of 9.3 was obtained. There was no ring sticking and the seals were in good condition.

An MWM-B test was conducted according to the CEC L-12-A-76 Test Method. The crankcase lubricant contained a formulation of the type utilised in the Sequence VE Test except that the dispersant was a compound of this invention formed as in Example 7. A piston merit value of 75 was achieved (passing value = 65). A crankcase lubricant formulated for diesel engine service and containing 5.8% by weight of a dispersant of this invention formed as in Example 4 gave in the same test procedure a piston merit value of 74.

A Petter W-1 Test was conducted using the CEC L-02-A-78 Test Procedure. A bearing weight loss of 5.7 mg was obtained using a crankcase lubricating oil formulation in which the dispersant was produced as in Example 7.

It will thus be seen that highly effective crankcase lubricant formulations can be formed utilising the dispersant compositions of this invention.

Additive concentrates of this invention generally contain 10-95 weight percent of one or more ashless dispersants of this invention, 0-90 weight percent liquid diluent and 0-90 weight percent of other additives commonly employed in lubricants and functional fluids.

5 The dispersants utilised according to the invention can be incorporated in a wide variety of lubricants. They can be used in lubricating oil compositions, such as automotive crankcase lubricating oils, automatic transmission fluids, or gear oils in effective amounts to provide active ingredient concentrations in finished formulations generally within the range of 0.5-10 weight percent, for example, 1-9 weight percent, preferably 2-8 weight percent, of the total composition. Conventionally, the dispersants are admixed with the lubricating oils as dispersant solution concentrates which usually contain up to about 50 weight percent of the active ingredient additive compound dissolved in mineral oil, preferably a mineral oil having an ASTM D-445 viscosity of 2-40, preferably 3-12 centistokes at 100°C.

10 The lubricating oil not only can be hydrocarbon oils of lubricating viscosity derived from petroleum but also can be natural oils of suitable viscosities such as rapeseed oil, etc., and synthetic lubricating oils such as hydrogenated polyolefin oils; poly- α -olefins (e.g., hydrogenated or unhydrogenated α -olefin oligomers such as hydrogenated poly-1-decene); alkyl esters of dicarboxylic acids; complex esters of dicarboxylic acid, polyglycol and alcohol; alkyl esters of carbonic or phosphoric acids; polysilicones; fluorohydrocarbon oils; and mixtures of lubricating oils and synthetic oils in any proportion. The term "lubricating oil" for this disclosure includes all the foregoing. The useful dispersant may be conveniently dispersed as a concentrate of 10-80 weight percent of mineral oil, e.g., Solvent 100 Neutral oil with or without

15 other additives being present and such concentrates are a further embodiment of this invention.

Other additives which may be included in the lubricants, functional fluids and additive concentrates of this invention include such substances as zinc dialkyl (C_3 - C_{10}), dicycloalkyl (C_5 - C_{20}), and/or diaryl (C_6 - C_{20}) dithiophosphate wear inhibitors, generally present in amounts of 0.5-5 weight percent. Useful detergents include the oil-soluble normal basic or overbased metal, e.g., calcium, magnesium, and barium salts of petroleum naphthenic acids, petroleum sulfonic acids, alkylbenzene sulfonic acids, oil-soluble fatty acids, alkyl salicylic acids, sulphurised or unsulphurised alkyl phenates, and hydrolysed or unhydrolysed phosphosulphurised

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polyolefins. Gasoline engine crankcase lubricants typically contain, for example, 0.5-5 weight percent of one or more detergent additives. Diesel engine crankcase oils may contain substantially higher levels of detergent additives. Preferred detergents are the calcium and magnesium normal or overbased phenates, sulphurised phenates or sulfonates.

Pour point depressants which may be present in amounts of 0.01-1 weight percent in the lubricant or functional fluid include wax alkylated aromatic hydrocarbons, olefin polymers and copolymers, and acrylate and methacrylate polymers and copolymers.

Viscosity index improvers, the concentrations of which may vary in the lubricants from 0.2 to 15 weight percent, (preferably 0.5-5 weight percent) depending on the viscosity grade required, include hydrocarbon polymers grafted with, for example, nitrogen-containing monomers, olefin polymers such as polybutene, ethylene-propylene copolymers, hydrogenated polymers and copolymers and terpolymers of styrene with isoprene and/or butadiene, polymers of alkyl acrylates or alkyl methacrylates, copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate, post-grafted polymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine, styrene/maleic anhydride polymers post-treated with alcohols and amines, etc.

Antiwear activity can be provided by 0.01-2 weight percent in the oil of the aforementioned metal dihydrocarbyl dithiophosphates and the corresponding precursor esters, phosphosulphurised pinenes, sulphurised olefins and hydrocarbons, sulphurised fatty esters and alkyl polysulphides. Preferred are the zinc dihydrocarbyl dithiophosphates which are salts of dihydrocarbyl esters of dithiophosphoric acids.

Other additives include effective amounts of friction modifiers or fuel economy additives such as the alkyl phosphonates as disclosed in U.S. 4,356,097, aliphatic hydrocarbyl substituted succinimides as disclosed in EPO 0020037, dimer acid esters, as disclosed in U.S. 4,105,571, oleamide, etc., which are present in the oil in amounts of 0.1-5 weight percent. Glycerol oleates are another example of fuel economy additives and these are usually present in very small amounts, such as 0.05-0.2 weight percent based on the weight of the formulated oil.

Antioxidants are also usually employed in the additive concentrates

and lubricants and functional fluids of this invention. Preferred are hindered phenolic antioxidants, methylene bridged alkylphenols, secondary aromatic amines, sulphurised phenols, alkyl phenothiazines, substituted triazines and ureas, and copper compounds such as copper naphthenate and copper oleate, among others. Typically the oil of lubricating viscosity will contain 0.001-2.5 weight percent of antioxidant. Particularly preferred are combinations of (i) at least one oil-soluble mononuclear monohydric phenol having a tertiary alkyl group in at least one position ortho to the hydroxyl group and a hydrogen atom or a tertiary alkyl group in the position para to the hydroxyl group, (ii) at least one oil-soluble methylene-bridged tertiary alkyl-substituted polyphenol, and (iii) at least one oil-soluble aromatic secondary amine, the proportions of (i), (ii) and (iii) being such that the weight percentage of nitrogen in component (iii) relative to the total weight of components (i), (ii) and (iii) is in the range of 0.05%-1.5%, and the weight ratio of monohydric phenols:methylene-bridged polyphenols in the composition is in the range of 15:1 to 1:2. Preferably component (i) in the foregoing composition is an oil-soluble mixture of said mononuclear monohydric phenols. It is likewise preferred that component (ii) of the foregoing composition be an oil-soluble mixture of said methylene-bridged tertiary alkyl-substituted phenols.

Particularly preferred is an antioxidant composition which comprises a combination of (i) an oil soluble mixture of sterically-hindered tertiary alkylated monohydric phenols, (ii) an oil-soluble mixture of sterically-hindered tertiary alkylated methylene-bridged polyphenols, and (iii) at least one oil-soluble aromatic secondary amine, the proportions of (i), (ii) and (iii) being such that the weight percentage of nitrogen in component (iii) relative to the total weight of components (i), (ii) and (iii) is 0.05%-1.5%, preferably 0.1%-0.8%, and most preferably 0.3%-0.7%, and the weight ratio of monohydric phenols:methylene-bridged polyphenols in the composition is in the range of 15:1 to 1:2, preferably in the range of 10:1 to 1:1, and most preferably in the range of 5:1 to 1:1. Preferred secondary aromatic amines are alkyl diphenylamines containing 1 or 2 alkyl substituents each having up to about 16 carbon atoms, phenyl- α -naphthylamine, phenyl- β -naphthylamine, alkyl- or aralkyl-substituted phenyl- α -naphthylamine containing 1 or 2 alkyl or aralkyl groups each having up to about 16 carbon atoms, alkyl- or aralkyl-substituted phenyl- β -naphthylamine containing 1 or 2 alkyl or aralkyl groups each having up to about 16 carbon atoms, and similar compounds. One such preferred

compound is available commercially as Naugalube 438L, a material which is understood to be predominantly a 4,4'-dinonyldiphenylamine (i.e., bis(4-nonylphenyl)amine) wherein the nonyl groups are branched.

5 Other well known components such as rust inhibitors, wax modifiers, foam inhibitors, copper passivators, sulphur scavengers, seal swell agents, color stabilisers, and like materials can be included in the compositions of this invention, provided of course that they are compatible with the ashless dispersant of this invention and the other component or components being employed.

10 This invention also includes among its embodiments improved methods of lubricating mechanical parts in the presence of at least one fluoroelastomer surface. In the practise of such methods, the lubrication is effected by means of a lubricating oil or functional fluid containing an ashless dispersant of this invention. The practise of such methods results in a lower -- oftentimes a substantially lower -- amount of degradation of the fluoroelastomer contacted by the
15 lubricating oil or functional fluid containing such ashless dispersant as compared to the amount of degradation that would occur under the same conditions using the same oil or fluid composition containing the same total quantity of the corresponding initial untreated ashless dispersant.

20 In another of its forms this invention provides ~~in combination, (a)~~ ^{comprising (a)} a mechanical mechanism ~~containing~~ moving parts to be lubricated, (b) a lubricating oil or functional fluid composition for lubricating such parts, and (c) a fluoroelastomer in contact with at least a portion of such lubricating oil or functional fluid during operation of such mechanism, characterised in that the lubricating oil or functional fluid composition for effecting such lubrication contains an ashless
25 dispersant of this invention. Such utilisation of this invention results in improvements in fluoroelastomer compatibility and enhanced antiwear performance, especially under actual service conditions. Among the mechanical mechanisms and systems lubricated in this manner are the crankcases of internal combustion engines; vehicular transmissions; hydraulic systems; hypoid axles; mechanical steering drives
30 in passenger cars, in trucks, and in cross-country vehicles; planetary hub reduction axles and transfer gear boxes in utility vehicles such as trucks; pinion hub reduction gear boxes; synchromesh and synchroniser type gear boxes; power take-off gears; and limited slip rear axles. The ashless dispersant can also be utilised in metal working,



machining, and cutting oils such as are applied to work pieces during cutting and shaping operations.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. An oil soluble dispersant composition formed by reacting a basic nitrogen-containing ashless dispersant (i) with at least one dibasic acylating agent containing
5 up to 12 carbon atoms per molecule and (ii) with at least one boron compound, said reactions (i) and (ii) being conducted concurrently or sequentially in any order such that the ashless dispersant is chemically modified via acylation in (i) and by boronation in (ii).
- 10 2. A composition in accordance with claim 1 wherein said dibasic acylating agent is maleic anhydride, maleic acid, fumaric acid, malic acid or any combination of any two, any three or all four of these compounds.
- 15 3. A composition in accordance with claim 1 or claim 2 wherein said boron compound is boric acid.
- 20 4. A lubricating oil or functional fluid composition comprising a major proportion of an oil of lubricating viscosity and a minor dispersant amount of the dispersant composition of any one of claims 1 to 3.
5. An additive concentrate containing the dispersant composition of claim 1.
- 25 6. A process which comprises reacting a basic nitrogen-containing ashless dispersant with at least one dibasic acylating agent having up to 12 carbon atoms in the molecular and with at least one boron compound, such reactions being conducted concurrently or sequentially in any order such that the ashless dispersant is chemically modified via acylation and boronation.
- 30 7. A process in accordance with claim 6 wherein said dibasic acylating agent is maleic anhydride, maleic acid, fumaric acid, malic acid or any combination of any two, any three or all four of these compounds.



8. A process in accordance with claim 6 or claim 7 wherein said boron compound is boric acid.

9. A method of lubricating mechanical parts in the presence of at least one
5 fluoroelastomer surface wherein the lubrication is effected by means of a lubricating oil or functional fluid containing the dispersant composition of any one of claims 1 to 3.

10. A mechanical mechanism comprising (a) moving parts to be lubricated, (b)
10 a lubricating oil or functional fluid composition for lubricating such parts, and (c) a fluoroelastomer in contact with at least a portion of such lubricating oil or functional fluid during operation of such mechanism, characterised in that the lubricating oil or functional fluid contains the dispersant composition of any one of claims 1 to 3.

15 11. Oil soluble dispersant compositions, methods for their manufacture, or concentrates or methods involving them, substantially as hereinbefore described with reference to the Examples.

20 DATED this 12th day of November, 1993.

ETHYL PETROLEUM ADDITIVES, LTD.

By Its Patent Attorneys

DAVIES COLLISON CAVE



MODIFIED DISPERSANT COMPOSITIONS

Abstract of the Disclosure

- 5 An oil soluble dispersant composition formed by reacting a basic nitrogen-containing ashless dispersant (i) with at least one dibasic acylating agent and (ii) with at least one boron compound, said reactions (i) and (ii) being conducted concurrently or sequentially in any order such that the initial ashless dispersant is chemically modified via acylation in (i) and by boronation in (ii).