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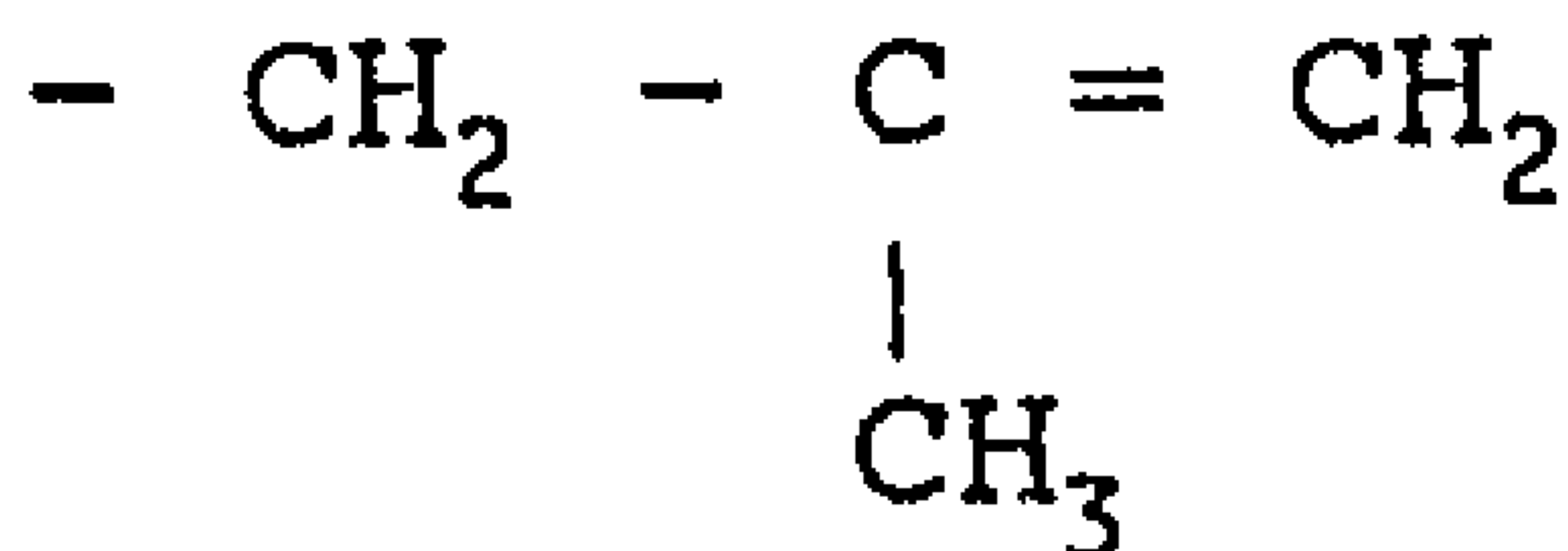
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(54) Titre : AGENTS DISPERSANTS SANS CENDRE OBTENUS A PARTIR D'AGENTS ACYLANTS DE SUBSTITUTION,
PRODUCTION ET UTILISATION

(54) Title: ASHLESS DISPERSANTS FORMED FROM SUBSTITUTED ACYLATING AGENTS AND THEIR
PRODUCTION AND USE



(57) **Abrégé/Abstract:**

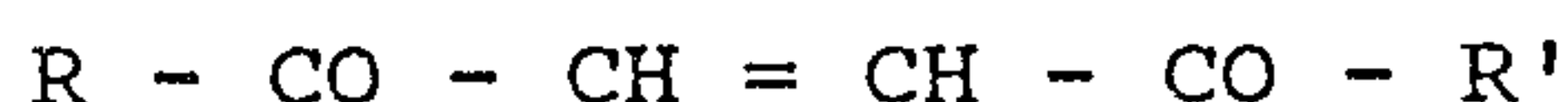
Succinic ester-amides are formed by (A) reacting (i) at least one substantially aliphatic polymer of at least one lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula R-CO-CH=CH-CO-R' wherein R and R' are independently -OH, -o-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process being characterized in that: a) the substantially aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the polyisobutene content of such polymer having an end group represented by the formula (see above formula) b) the mole ratio of said acidic reactant(s): said polymer(s) is at least 1 : 1; c) the reaction mixture is maintained under superatmospheric pressure during at least a substantial portion of the reaction period; and d) said acylating agent is characterized by having an average total tar rating as determined by the method described in the specification hereof that is at least 25% lower than the average total tar rating of a corresponding product made in the same way under the same reaction conditions using a polyisobutene containing up to 10% of the above-depicted end group; and (B) reacting such acylating agent with at least one alcohol (preferably a polyhydric alcohol) and amine (preferably a polyamine having at least one primary amino group). Combinations of succinimides, succinic esters, and succinic ester-amides formed using such acylating agents are used in combination with other additives in forming lubricant compositions.



ASHLESS DISPERSANTS FORMED FROM
SUBSTITUTED ACYLATING AGENTS AND THEIR PRODUCTION AND USE

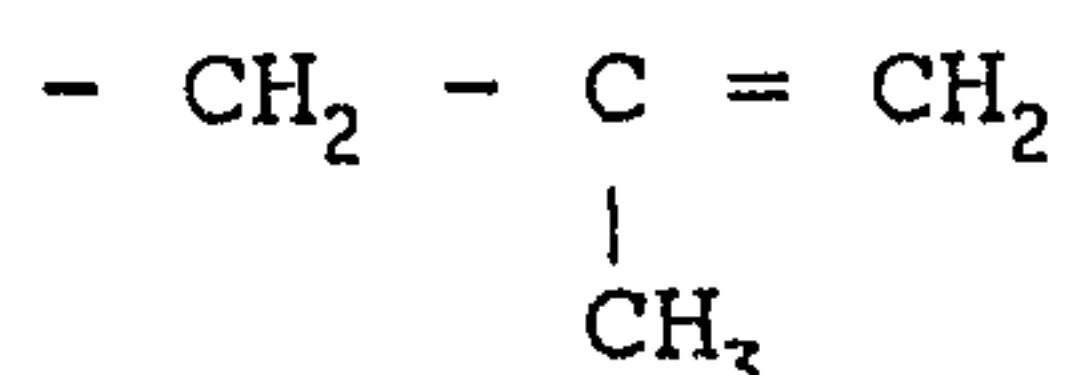
Abstract of the Disclosure

Succinic ester-amides are formed by (A) reacting (i) at least one substantially aliphatic polymer of at least one lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula



wherein R and R' are independently -OH, -O-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process being characterized in that:

- a) the substantially aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the polyisobutene content of such polymer having an end group represented by the formula



- b) the mole ratio of said acidic reactant(s) : said polymer(s) is at least 1 : 1;
- c) the reaction mixture is maintained under superatmospheric pressure during at least a substantial portion of the reaction period; and
- d) said acylating agent is characterized by having an average total tar rating as determined by the method described in the specification hereof that is at least 25% lower than the average total tar rating of a corresponding product made in the same way under the same reaction conditions using a polyisobutene containing up to 10% of the above-depicted end group; and

(B) reacting such acylating agent with at least one alcohol (preferably a polyhydric alcohol) and amine (preferably a polyamine having at least one primary amino group). Combinations of succinimides, succinic esters, and succinic ester-amides formed using such acylating agents are used in combination with other additives in forming lubricant compositions.

ASHLESS DISPERSANTS FORMED FROM
SUBSTITUTED ACYLATING AGENTS AND THEIR PRODUCTION AND USE

This invention relates to novel and eminently useful ashless dispersants formed from substituted acylating agents of the polybutenylsuccinic acid type, to novel and eminently useful methods for their production, and to novel and eminently useful compositions in which they are used.

Heretofore processes have been described for the thermal reaction between polybutenes (predominantly polyisobutenes) and maleic anhydride or like reactants whereby polybutenyl succinic anhydrides are formed. Some of the work along these lines is described, or at least referred to, for example in U. S. Pat. Nos. 3,018,247; 3,018,250; 3,018,291; 3,172,892; 3,184,474; 3,185,704; 3,194,812; 3,194,814; 3,202,678; 3,216,936; 3,219,666; 3,272,746; 3,287,271; 3,311,558; and in British Pat. No. 1 492 337. However as pointed out in U. S. Pat. Nos. 3,215,707 and 3,231,587, from the standpoint of commercial usefulness the alkylation of maleic anhydride with an olefinic hydrocarbon is very time-consuming and limited in its applicability to relatively low molecular weight olefinic hydrocarbon reactants, i.e., those having less than about 12-15 carbon atoms. These two patents further state that the higher molecular weight olefinic hydrocarbons are apparently not sufficiently reactive with maleic anhydride to be useful as an acylating agent, and that higher molecular weight hydrocarbon-substituted succinic acid compounds are almost invariably prepared by reacting maleic anhydride with a halogenated high molecular weight hydrocarbon reactant. Indeed, in U. S. 4,234,435 it is reported that the process as described in these two patents is presently deemed best for preparing the substituted succinic acylating agents.

British Pat. No. 1 492 337 points out that while such acylating agents can be prepared by thermally reacting a polymer having an average molecular weight above about 200 with maleic anhydride at a temperature above 200°C, the reaction rate of such reactions is low and that attempts to improve the reaction rate by increasing the temperature and/or by using superatmospheric pressure results in degradation of maleic anhydride to useless carbon dioxide, water and tarry solids.

U. S. Pat. No. 3,476,774 reports in Example 1 that reaction under nitrogen between polybutene and maleic anhydride conducted in a pressure vessel at 234°C-236°C for 6 hours and 40 minutes in o-dichlorobenzene solvent gave an alkenyl succinic anhydride product

that had particles of sludge suspended in it. Improvements in yield are reported in Examples 2-4 of the patent wherein a thermal stabilizer (4,4'-methylenebis(2,6-di-tert-butyl-phenol)) was incorporated in the reaction mixture.

5 U. S. Pat. No. 4,883,886, in discussing the addition reaction between viscous polyalkenes and anhydride reactants such as maleic anhydride, states that a known problem frequently encountered in this reaction is thermal decomposition and polymerization of the unsaturated anhydride reactant at temperatures above about 150°C. According to the patentee, such thermal decomposition is accom-
10 panied by evolution of water vapor and oxides of carbon, and in a closed reaction vessel is accompanied by an increase in internal pressure. The patentee continues:

"Under some observed conditions, the thermal decomposition can
15 be so rapid as to be explosive. In the absence of explosive thermal decomposition, a carbon-containing tarry residue is also formed in addition to water vapor and oxides of carbon.

* * * Such thermal decomposition and attendant isomerization or polymerization of the unsaturated anhydride reactant has
20 been observed as occurring during its addition reaction with polymeric olefins, e.g., polybutenes and others, in a closed reaction vessel. The carbon-containing residue varies in nature from somewhat granular when the decomposition is only slight to a tarry material mainly adhering to internal sur-
25 faces of the reaction vessel when the decomposition is more extensive but well below explosive magnitude. The granular type residue amounts to about from 0.1 to about 0.3 weight percent of the total charge and is generally dispersed in the alkenyl-substituted saturated anhydride addition compound
30 product diluted with unreacted components of the olefin polymer, and is readily separated therefrom by filtration. However, the tarry residue product, which for the most part fouls the internals of the reaction vessel can be as high as 2-3 weight percent of the total charge. The tarry material
35 not adhering to the internal surfaces of the reactor fouls the filter and interferes with filtration of the desired reaction product. Both types of residue are undesirable because of the above noted fouling characteristics and because their formation results in yield reduction of the desired alkenyl-substi-
40 tuted anhydride addition product."

The patentee refers to a number of other patents describing catalysts or agents which decrease such unwanted by-product formation, and utilizes such materials in a particular process in order to suppress the formation of tars and undesired side products.

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U. S. Pat. No. 4,152,499 discloses that polybutenes having a higher proportion of terminal double bonds than conventional polybutenes can be produced by polymerizing isobutene with boron trifluoride as the initiator, if (a) the polymerization is carried out at -50°C to +30°C, (b) from 1 to 20 mmoles of boron trifluoride are used per mole of isobutene, and (c) the mean polymerization time is confined to from 1 to 10 minutes. The patent further discloses that such polybutenes can be reacted with the stoichiometric amount of maleic anhydride, or a slight excess thereof, "in the conventional manner" at from 170°C to 250°C, and that such polybutenes when heated with maleic anhydride for 4 hours at 200°C with stirring, followed by removing excess maleic anhydride under greatly reduced pressure exhibited a substantially greater activity than two commercial isobutene polymers. W. German Offenlegungsschrift 29 04 314 teaches the desirability of conducting the polymerization of the isobutene in the same manner except using a polymerization time limited to 1 to 40 seconds, and that to prepare mineral oil additives, "the polyisobutene is reacted in known fashion with the stoichiometric amount or a slight excess of maleic acid anhydride at 170 to 250°C."

It has also been disclosed heretofore that a specified thermal maleinisation reaction can be used to assess the quality (reactivity) of a polybutene polymer. In this procedure polybutene (50g) is reacted with maleic anhydride (9.8g), a 1:2 mole ratio, for 24 hours in a stirred reaction tube immersed in a bath of specified hydrocarbons under reflux at 210°C. The reaction is conducted under nitrogen, and the reaction mixture is stirred at a specified number of revolutions per minute. A specifically designed apparatus is suggested for use in this procedure. The procedure results in the formation of both polybutenyl succinic anhydride and a complex resinous co-product formed from maleic anhydride.

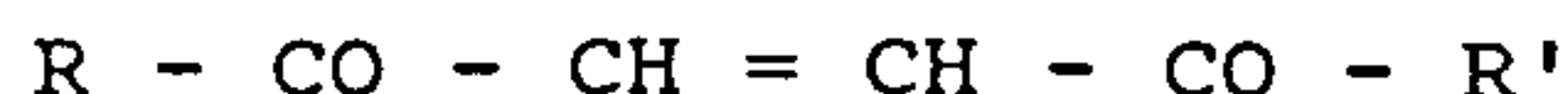
As disclosed in U.S. Patent No. 5,071,919, it has been found that substantial advantages can be realized by reacting an acidic reactant, such as maleic anhydride, with a substantially aliphatic polymer composed principally or entirely of polyisobutene in a mole ratio of acidic reactant(s) : polymer is at least 1 : 1, provided that at least 50% (preferably at least 75%) of the polyisobutene content of such polymer has an end group represented by the formula



and the reaction mixture is maintained under superatmospheric pressure during at least a substantial portion of the reaction period. Most preferably, the polymer consists essentially of polyisobutene (i.e., it contains at least 50 mole % and more preferably at least 60 mole % of polymerized isobutene) and at least 50% (more desirably at least 75%) of the total polymer(s) is polyisobutene having such end group.

This invention provides in one of its embodiments novel and eminently useful ashless dispersants prepared by use of the substituted acylating agents formed as described in U.S. Patent No. 5,071,919. More particularly, the so-formed polybutenyl succinic acids or acid derivatives thereof (polybutenyl succinic anhydrides, polybutenyl succinic acid halides, polybutenyl succinic acid lower alkyl esters) are especially useful in the manufacture of polybutenyl succinic ester-amides by reaction with alcohols and amines. The amines are preferably alkylene polyamines such as ethylene or propylene diamines, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, etc. The alcohols are preferably polyhydric alcohols. Such polybutenyl succinic esteramides are especially useful as ashless dispersants in lubricating oils and functional fluids.

One embodiment of this invention provides a carboxylic derivative composition produced by reacting (A) at least one substituted succinic acylating agent with (B) a combination of at least one amine having at least one primary or secondary amino group and at least one alcohol, the components of (B) being reacted with said at least one substituted succinic acylating agent concurrently or sequentially in any order, said at least one succinic acylating agent being prepared by reacting (i) at least one substantially aliphatic polymer of at least one lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula



wherein R and R' are independently -OH, -O-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process of preparing said at least one succinic acylating agent being characterized in that:

- a) the substantially aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the polyisobutene content of such polymer having an end group represented by the formula



- 5 b) the mole ratio of said acidic reactant(s) : said polymer(s) is at least 1 : 1; and
- c) the reaction mixture is maintained under superatmospheric pressure during at least a substantial portion of the reaction period.
- 10 Generally speaking, the carboxylic derivative compositions of this invention are formed from acylating agents having an average total tar rating as determined by the method described in the specification hereof that is at least 25% lower than the average total tar rating of a corresponding acylating agent made in the same way
- 15 under the same reaction conditions using a polyisobutene containing up to 10% of the above-depicted end group. Preferred acylating agents used in forming the carboxylic derivative compositions of this invention are characterized by having an average total tar rating as determined by the method described in the specification
- 20 hereof that is at least about 40% lower (for example about 43% lower) and most preferably at least 50% lower than the average total tar rating of a corresponding product made in the same way under the same reaction conditions using a polyisobutene containing less than 10% of the above-depicted end group. In this connection
- 25 it will be appreciated that such terms as "total tars value", "average total tars", "total tar content" and "total tars" are alternative ways of referring to the average total tar rating, since all such terms or expressions refer to the numerical result obtained by use of the method described in the specification
- 30 hereof.

 Particularly preferred acylating agents of the types described above have a succination ratio of less than 1.3 -- i.e., the acylating agents have within their structure an average of less than 1.3 succinic groups per each substituent group derived from the afore-

35 said substantially aliphatic polymer.

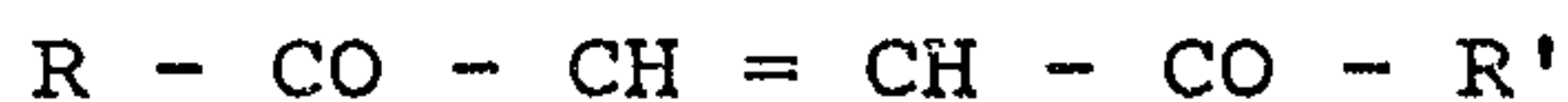
 Another embodiment of this invention involves the process of forming a carboxylic derivative composition which comprises reacting (A) at least one substituted succinic acylating agent with (B) a combination of at least one amine having at least one primary or

40 secondary amino group and at least one alcohol, the components of (B) being reacted with said at least one substituted succinic acylating agent concurrently or sequentially in any order, said at least one succinic acylating agent having been prepared as

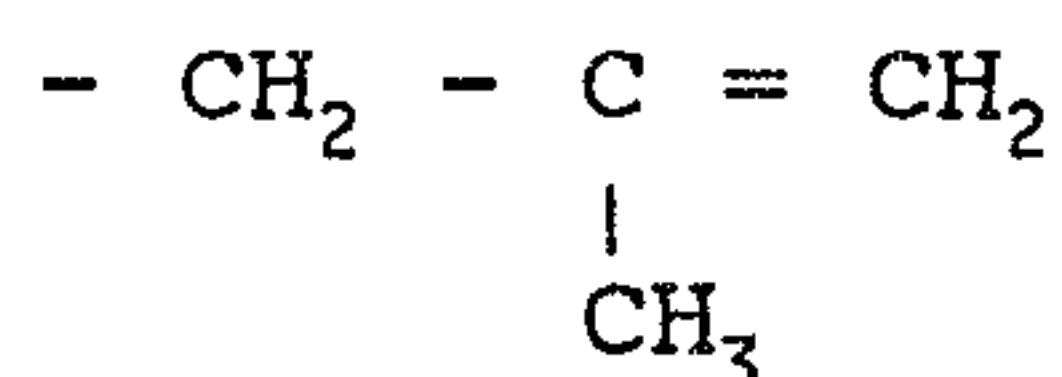
described above. The preferred acylating agents of this type for use in the process are characterized by having an average total tar rating as determined by the method described in the specification hereof that is at least about 40% lower (for example about 43% lower) and most preferably at least 50% lower than the average total tar rating of a corresponding product made in the same way under the same reaction conditions using a polyisobutene containing less than 10% of the above-depicted end group. Particularly preferred acylating agents of this type have a succination ratio of less than 1.3.

A further embodiment of this invention relates to a two-stage process for the production of a carboxylic derivative composition and to the novel products formed thereby. Pursuant to this embodiment, a carboxylic derivative composition is produced by a process which comprises:

A. reacting (i) at least one substantially aliphatic polymer of at least one lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula



wherein R and R' are independently -OH, -O-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process of preparing said acylating agent being characterized in that a) the substantially aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the polyisobutene content of such polymer having an end group represented by the formula



b) the mole ratio of said acidic reactant(s) : said polymer(s) is at least 1 : 1; and c) the reaction mixture is maintained under superatmospheric pressure during at least a substantial portion of the reaction period, whereby a substituted succinic derivative composition is formed; and

B. reacting (1) said substituted succinic acylating agent with (2) a combination of at least one amine having at least one primary or secondary amino group and at least one alcohol, the components of (2) being reacted with said at least one substituted succinic acylating agent concurrently or sequentially in any order.

Pursuant to a preferred embodiment of this two-stage process, the substituted succinic derivative composition formed in Stage A and used in Stage B has an average total tar rating as determined by the method described in the specification hereof that is at least about 40% lower (for example about 43% lower) and most preferably at least 50% lower than the average total tar rating of a corresponding product made in the same way under the same reaction conditions using a polyisobutene containing less than 10% of the above-depicted end group. Particularly preferred acylating agents of this type have a succination ratio of less than 1.3.

The carboxylic derivative compositions of this invention formed as described above have a good balance of oxidative and thermal stability, and thus can be subjected to more stringent thermooxidative conditions than corresponding products made in the same way under the same reaction conditions using a polyisobutene containing less than 10% of the above-depicted end group.

Also provided by this invention are carboxylic derivative compositions produced as above which are further reacted with one or more post-treating reactants such as the following: an inorganic phosphorus acid or anhydride; a water-hydrolyzable organic phosphorus compound and water; an organic phosphorus compound; phosphorus pentasulfide; a boron compound; a mono- or polycarboxylic acid, anhydride or acid halide; a mono- or polyepoxide or thioepoxide; an aldehyde or ketone; carbon disulfide; glycidol; urea, thiourea or guanidine; an organic sulfonic acid; an alkenyl cyanide; diketene; a diisocyanate; an alkane sultone; a 1,3-dicarbonyl compound; a sulfate of an alkoxylated alcohol or alkoxylated phenol; a cyclic lactone; a cyclic carbonate or thiocarbonate, a linear monocarbonate or polycarbonate, or chloroformate; a nitrogen-containing carboxylic acid; a hydroxy-protected chlorodicarbonyloxy compound, a lactam, thiolactam, thiolactone or dithiolactone; a cyclic carbamate, cyclic thiocarbamate or cyclic dithiocarbamate; a hydroxyaliphatic carboxylic acid; an oxidizing agent; the combination of phosphorus pentasulfide and a polyalkylene polyamine; the combination of a carboxylic acid or an aldehyde or ketone and sulfur or sulfur chloride; the combination of an aldehyde and a phenol; the combination of an aldehyde and an O,O-diester of dithiophosphoric acid; the combination of a hydroxyaliphatic carboxylic acid and a boric acid; the combination of a hydroxyaliphatic acid, then formaldehyde and a phenol; the combination of a hydroxyaliphatic acid and then a dicarboxylic acid; the combination of formaldehyde and a phenol, and then glycolic acid; the combination of a hydroxyaliphatic carboxylic acid or oxalic acid and then a diisocyanate; the

combination of an inorganic acid or anhydride of phosphorus or a partial or total sulfur analog thereof and a boron compound; the combination of an organic diacid, then an unsaturated fatty acid, and then a nitroso-aromatic amine, optionally followed by a boron compound and optionally followed by glycolic acid; the combination of an aldehyde and a triazole; the combination of an aldehyde and a triazole, then a boron compound; and the combination of cyclic lactone and a boron compound. The fact that such a vast array of post-treating agents can be used does not signify that they are equivalent to each other in every instance. For example, some of the foregoing post-treating agents improve the antiwear properties of succinimides, succinic esters, and/or succinic ester-amides made using the acylating agents as described in U.S. Patent No. 5,071,919. Examples are the inorganic phosphoric acids or anhydrides, and the water-hydrolyzable organic phosphorus compounds and water, when used in combination (concurrently or sequentially) with a boron compound. Other post-treating agents have no appreciable effect on antiwear performance but are effective in improving other properties such as passivity toward polymeric materials used in fabricating seals, diaphragms, and other components with which oils of lubricating viscosity frequently come in contact during actual service conditions.

Still further embodiments of this invention relate to the provision of novel and eminently useful compositions wherein carboxylic derivative compositions, whether or not post-treated as above, are utilized in combination with one or more other components, especially zinc hydrocarbyl dithiophosphates, Group I or II metal detergent compositions, active sulfur-containing antiwear and/or extreme pressure agents, and/or metal-free phosphorus-containing antiwear and/or extreme pressure agents.

Succinic Acylating Agents

The succinic acylating agents utilized in forming the carboxylic acid derivative compositions are formed as described in Published European Patent Application, Publication No. 0457,599 and U.S. Pat. No. 5,071,919. Accordingly, reference should be had to that published patent application for further details concerning the production of the succinic acylating agents.

Methods for producing polybutenes useful in the practice of this process are described in U.S. Pat. No. 4,152,499 and in W. German Offenlegungsschrift 29 04 314. Suitable products are understood to be available under the trade designation "Ultravis".

Table 1 summarizes the total tar content and the stripped acid number (i.e., the acid number of the residual product after stripping) of the respective products of Examples 1-5, and provides a comparison of the corresponding values on a product made under the same general reaction conditions (including superatmospheric pressure) using a PIB that contained less than 10% of the above-depicted end group, and wherein the mole ratio (MA:PIB) was 1:1.

The procedure for determination of total tar content used herein is as follows: After completion of the reaction run, the reactor head and attached agitator are removed, and the reactor contents are transferred from the autoclave to storage and analysis bottles. The appearance of the reactor and its component parts is immediately rated by at least two, and preferably three, trained technical personnel. The rating takes place in a specific manner, namely:

1) Each of the three major internal components of the autoclave -- i.e., the sides, the bottom, and the agitator, is independently rated.

2) The rating is based upon the visual appearance of the component and the amount of tar present. The rating scale ranges from 1 to 10, with "1" representing a perfectly clean component showing no evidence of tar formation. The rating of "10" represents a heavily tarred component which is completely covered with tar. In general, an intermediate rating corresponds to the area of the surface covered by the black tar. For example, a rating of "7" means that approximately 70% of the surface is covered with tar.

3) Each person making the evaluations works independently of the other person(s) and thus records his/her observations without consultation with, or knowledge of the ratings made by, the other person(s).

4) The rating numbers for the three individual components are added together for each individual evaluator and the sum of all of these totals are averaged (i.e., divided by the number of evaluators) to yield an average total tar rating reported herein.

5) The average total tar rating scale is as follows:

3 to 5	-	Excellent; very clean reactor, tar formation minimal or non-existent
6 to 10	-	Good; some tar formation
11 to 14	-	Fair; significant level of tar formation
15 to 20	-	Poor; medium to heavy tar formation
20 to 30	-	Very Poor; heavy to severe tar formation

Table 1 - Key Properties of Polyisobutenyl Succinic Anhydrides

<u>Example</u>	<u>Reaction Temperature</u>	<u>MA:PIB Ratio</u>	<u>Maximum Pressure</u>	<u>Total Tars</u>	<u>Stripped Acid No.</u>
1	225°C	1.00	13.0 psig	4	0.76
2	240°C	1.00	17.0 psig	4	0.82
5 3	225°C	1.10	14.5 psig	3	0.81
4	240°C	1.10	34.0 psig	3	0.90
5	240°C	1.20	21.0 psig	3	0.95
Control	225°C	1.00	15.0 psig	7	0.60

10 As shown by data presented in Table 1, the average total tar rating of the PIBSA made in Example 1 was 43% lower than the average total tar rating of the PIBSA made in the same way under essentially the same reaction conditions using a polyisobutene containing less than 10% of the end group depicted hereinabove.

15 More recent experimental work than that presented in Published European Patent Application No. 457,599 A2 provided additional confirmation of this advantageous result. For example, two runs (Examples 11 and 12) were conducted generally as in Example 4 using a polyisobutene from a different supplier that had a number average molecular weight (by GPC) of 1323 and that contained approximately 20 73% of polymer having the end group depicted hereinabove (as indicated by the supplier). A control run was conducted in the same manner using a polyisobutene having a number average molecular weight of 1314 (by GPC) but which contained at most only 15% of polymer with such end group. In each such run the reaction was 25 conducted for 5 hours at 240°C utilizing a 1.10 molar ratio of maleic anhydride to polyisobutene. Table 2 summarizes the results obtained, including the average total tar ratings on the products.

Table 2 - Results of Comparative Runs

<u>Example</u>	<u>Maximum Pressure</u>	<u>Total Tars</u>	<u>Unstripped Acid No.</u>	<u>Stripped Acid No.</u>	<u>Unreacted PIB, %</u>
11	13.8 psig	9.0	0.73	0.66	25.4
12	21.0 psig	9.7	0.73	0.64	23.3
Control	17.0 psig	19.0	0.70	0.53	40.3

35 From Table 2 it can be seen that the average total tar rating of the PIBSA made in Examples 11 and 12 averaged about 51% less than the average total tar rating of the PIBSA made in the control run.

Typically the difference in acid number of the reaction product before and after removal of residual acidic reactant(s) therefrom is no greater than 0.23, preferably no greater than 0.16, and most preferably is 0.10 or less.

5 As noted above, the polyolefin, most preferably polyisobutene, of the succinic acylating agent has a number average molecular weight of at least 500, and preferably has a number average molecular weight in the range of 700 to 5,000, and more preferably in the range of 800 to 2,500, and especially 800 to 1,300. In this connection, the reputable commercial manufacturers of such polyolefins
10 identify their products, inter alia, by means of number average molecular weights, and the designations provided by such suppliers can be relied upon.

Succinic Ester-Amides

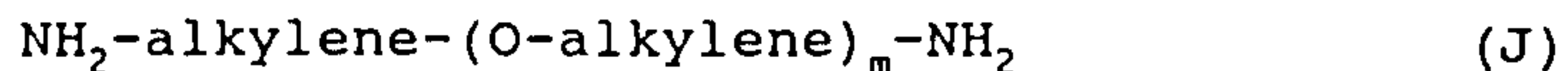
15 To form the alkenyl succinic ester-amides of this invention, the above-described alkenyl succinic acids, anhydrides or lower alkyl esters or etc. are heated with an alcohol and an amine either sequentially or in a mixture.

20 The amine reactants can be widely diverse in chemical structure, and include straight, branched chain, and cyclic amines which can be unsubstituted or substituted with other functional groups, such as one or more ester groups, ether linkages, carbonyl groups, oxirane groups, carboxyl groups, thioether linkages, sulfhydryl groups, hydroxyl groups, and many others.

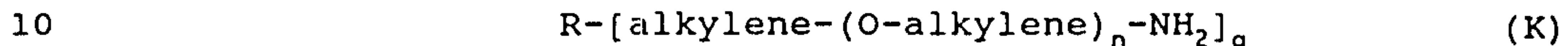
25 A few representative examples of amine reactants which may be employed in forming the ashless dispersants of this invention include straight or branched-chain alkanes containing two or more amino groups at least one of which is a primary amino group, such as 1,6-diaminooctane, 1,8-diaminooctane, 1,5,9-triaminononane,
30 tetraaminoneopentane, etc.; polyaminoalkanols such as 2-(2-aminoethylamino)-ethanol and 2-[2-(2-aminoethylamino)-ethylamino]-ethanol; heterocyclic compounds containing two or more amino groups at least one of which is a primary amino group such as 1-(β -aminoethyl)-2-imidazolidone, 2-(2-aminoethylamino)-5-nitropyridine, 3-amino-N-ethylpiperidine, 2-(2-aminoethyl)-pyridine, 5-aminoindole, 3-
35 amino-5-mercapto-1,2,4-triazole, and 4-(aminomethyl)-piperidine; the alkylene polyamines such as 1,2-propylene diamine, di-(1,2-propylene)triamine, di-(1,3-propylene)triamine, N,N-dimethyl-1,3-propanediamine, 1,4-butanediamine, di-(1,2-butylenetriamine, N-(2-aminoethyl)-1,3-propanediamine, hexamethylenediamine and tetra-
40 (1,2-propylene)pentamine; the hydroxyamines such as tris(hydroxymethyl)aminomethane, isopropanol amine, N-(2-hydroxyethyl)-1,3-

propanediamine, N-2-hydroxypropyl ethylene diamine, N-aminoethyl-ethanolamine, 4-aminophenol: the aromatic polyamines such as p-phenylene diamine, etc.; and the like.

Other useful amines include polyoxyalkylene polyamines such as those depicted by the formulas



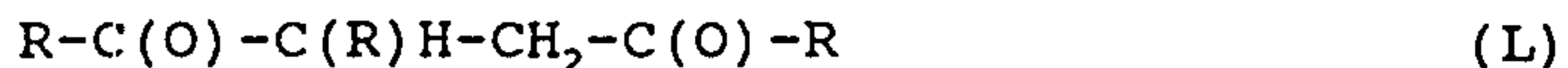
where the alkylene groups can be the same or different straight or branched chain groups containing 2 to 8 and preferably 2 to 4 carbon atoms each, and m is from 3 to 70 and preferably 10 to 35; and



where the alkylene groups can be the same or different straight or branched chain groups containing 2 to 8 and preferably 2 to 4 carbon atoms each, R is a substituted hydrocarbon group, usually a saturated hydrocarbon group, of up to 10 carbon atoms, q represents the number of the depicted substituents on R and is from 3 to 6, and n is from 1 to 40 with the proviso that the sum of the n 's is from 3 to about 70 and preferably from about 6 to about 35.

The polyoxyalkylene amines such as are depicted in Formula J or K, for example the polyoxyalkylene diamines and polyoxyalkylene triamines, may have various number average molecular weights, typically in the range of about 200 to about 4,000 and preferably in the range of about 200 to about 2,000. Polyoxyalkylene polyamines are available as articles of commerce, and may be obtained for example from the Jefferson Chemical Company, Inc. under the trade designations Jeffamine^{*} D,230, Jeffamine D-400, Jeffamine D-1000, Jeffamine D2000, Jeffamine T-403, etc.

Another group of polyoxyalkylene polyamines are those represented by the formula



wherein R is $\text{-NH-(alkylene-O)}_n\text{-alkylene-NH}_2$ and n is 2 or 3. The alkylene groups can be the same or different, straight or branched chain groups containing 2 to 8 and preferably 2 to 4 carbon atoms each. These compounds are formed by reacting 3 to about 3.5 moles of a dicarboxylic acid reactant such as maleic acid, fumaric acid, or their anhydrides or C_{1-4} dialkyl esters with a polyoxyalkylene diamine of the formula $\text{H}_2\text{N-(alkylene-O)}_n\text{-alkylene-NH}_2$ wherein alkylene and n are as just defined. Methods suitable for preparing such polyoxyalkylene polyamines are set forth for example in European Patent Publication No. EP 435,497.

*Trade-mark

Another type of amine reactants which can be used in forming the carboxylic derivatives of this invention are the amido-amine adducts such as are described in U.S. Pat. No. 5,034,018.

5 The most preferred amines are the ethylene polyamines which can be depicted by the formula



wherein n is an integer from one to about ten. These include: ethylene diamine, diethylene triamine, triethylene tetramine, 10 tetraethylene pentamine, pentaethylene hexamine, and the like, including mixtures thereof in which case n is the average value of the mixture. These ethylene polyamines have a primary amine group at each end so can form mono-alkenylsuccinimides and bis-alkenylsuccinimides. Commercially available ethylene polyamine mixtures 15 usually contain minor amounts of branched species and cyclic species such as N-aminoethyl piperazine, N,N'-bis(aminoethyl)piperazine, N,N'-bis(piperazinyl)ethane, and like compounds. The preferred commercial mixtures have approximate overall compositions falling in the range corresponding to diethylene triamine to pentaethylene hexamine, mixtures generally corresponding in overall 20 makeup to tetraethylene pentamine being most preferred. Various suitable low cost polyethylene polyamine mixtures are available under various trade designations such as "Polyamine H", "Polyamine 400", "Dow Polyamine E-100", "Dow S-1107", etc. Methods for the 25 production of polyalkylene polyamines are known and reported in the literature. See for example U.S. Pat. No. 4,827,037; 4,983,736; EP Nos. 412,611; 412,612; 412,613; 412,614; and 412,615, and references cited therein.

The alcohol and phenol reactants can be used singly or in 30 combinations, including combinations of monohydric alcohols, combinations of polyhydric alcohols, combinations of monohydric phenols, combinations of polyhydric phenols, combinations of at least one monohydric alcohol and at least one polyhydric alcohol, combinations of at least one monohydric phenol and at least one polyhydric phenol, combinations of at least one monohydric alcohol and at 35 least one polyhydric phenol, combinations of at least one polyhydric alcohol and at least one monohydric phenol, combinations of at least one monohydric alcohol, at least one polyhydric alcohol and at least one monohydric phenol, combinations of at least one monohydric alcohol, at least one polyhydric alcohol and at least one 40 polyhydric phenol, combinations of at least one monohydric phenol, at least one polyhydric phenol and at least one monohydric alcohol, combinations of at least one monohydric phenol, at least one polyhydric phenol and at least one polyhydric alcohol, and combinations of at least one monohydric alcohol, at least one polyhydric alco- 45

*Trade-mark

hol, at least one monohydric phenol and at least one polyhydric phenol. Polyhydric alcohols (often referred to as polyols) are the most preferred reactants for forming the ester-amides of this invention.

5 The alcohols can be widely diverse in chemical structure, and include straight and branched chain alcohols which can be unsubstituted or substituted with other functional groups, such as one or more ester groups, ether linkages, carbonyl groups, oxirane groups, carboxyl groups, thioether linkages, sulfhydryl groups, and many
10 others.

 Typical alcohols which can be used include ethylene glycol, diethylene glycol, tetraethylene glycol, diethylene glycol monoethylether, propylene glycol, tripropylene glycol, glycerol, sorbitol, monomethyl ether of glycerol, 1,1,1-trimethylol ethane,
15 1,1,1-trimethylol propane, 1,1,1-trimethylol butane, pentaerythritol, dipentaerythritol, tripentaerythritol, 9,10-dihydroxystearic acid, 3-chloro-1,2-propanediol, 1,2-butanediol, 2,3-hexanediol, pinacol, mannitol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, cyclohexanedimethanol, glucose, mannose, triethanolamine, trioctanolamine, erythritol, higher molecular weight
20 polyoxyalkylene glycols (e.g., polyoxyethylene glycols, polyoxypropylene glycols, mixed oxyethylene-oxypropylene glycols, etc.), glycerine-initiated polyoxyalkylene triols, and the like.

 Typical phenols which can be used include such compounds as
25 catechol, resorcinol, hydroquinone, tert-butylhydroquinone, 4-hydroxymethylphenol, 1,4-dihydroxynaphthalene, 4,4'-biphenol, 4,4'-methylenebisphenol, bisphenol-A, sym-trihydroxybenzene, 4-(1,1,3,3-tetramethylbutyl)catechol, 3,3',4,4'-tetrahydroxydiphenyl, 4-(dimethylamino)phenol, 4-(diethylaminomethyl)phenol, 4-(2-hydroxyethoxyethoxy)phenol, and many other similar compounds.
30

 Alternatively, amino alcohols and/or aminophenols can be used alone or with the alcohol and/or amine reactant to form ester-amide mixtures. The amino alcohol can contain up to 100 carbon atoms, 1-10 hydroxy groups and 1-6 amine nitrogen atoms. Examples are
35 ethanolamine, 2-amino-2-methyl-1-propanol, 4-(2-hydroxyethyl)aniline, 2-aminopropanol, diethanolamine, 3-amino-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, N-(2-hydroxypropyl)-N'-(2-aminoethyl)piperazine, tris(hydroxymethyl)aminomethane (also known as tris-
40 (methylol)aminomethane), 2-amino-1-butanol, N-ethanol-diethylene

triamine, and the like, including mixtures of two or more such substances.

The alkenyl group of the succinic ester-amide can be hydrogenated or subjected to other reactions involving olefinic double bonds.

A sub-category of carboxylic ashless dispersants of this invention comprises the Mannich-based derivatives of hydroxyaryl succinimides. Such compounds can be made by reacting a succinic acylating agent prepared as described above with an aminophenol to produce an N-(hydroxyaryl) hydrocarbyl succinimide which is then reacted with an alkylene diamine or polyalkylene polyamine and an aldehyde (e.g., formaldehyde), in a Mannich-base reaction. In conducting such a process, reaction conditions such as are set forth in U.S. Pat. No. 4,354,950, can be used except that the succinic acylating agent is formed as described above using a polyolefin, preferably a polyisobutene, having a number average molecular weight of 500 to 5,000, preferably 700 to 2,500, more preferably 700 to 1,400, and especially 800 to 1,200. Likewise, residual unsaturation in the polyalkenyl substituent group can be used as a reaction site as for example, by hydrogenation, sulfurization, or the like.

Reaction Conditions

The reaction between the succinic acylating agent and the amine reactant(s) and/or the alcohol reactant(s) is carried out under conventional reaction conditions. In preparing a succinimide at least 0.5 equivalent (i.e., 1 mole) of the acylating agent reacts per equivalent of reactive primary and/or secondary amino groups present in the amine reactant(s). For example, from 1 to 2 moles of the acylating agent can react with one mole of a diamine having two reactive primary amino groups (and thus two equivalents of reactive amino groups). Similarly, from 1 to 4 moles of the acylating agent can react with one mole of an amine having four reactive primary amino groups (and thus four equivalents of reactive amino groups). In preparing a succinic ester at least one mole of the acylating agent reacts per equivalent of reactive hydroxyl groups present in the alcohol reactant(s). For example, from 1 to 4 moles of the acylating agent can react with one mole of a diol having two reactive hydroxyl groups per molecule. Ester-amides of this invention are formed by suitably proportioning the amine reactant(s) and alcohol reactant(s) so as to form an acylated product in which at least some of the hydroxyl groups and at least some of the primary amino groups are acylated.

Thus the reactants are proportioned to achieve the desired extent of acylation in the product according to well known principles. With a polyalkylene polyamine having approximately two reactive primary amino groups per molecule the amount of succinic acylating agent used is generally such as to cause at least 1.6 succinic groups to react per molecule of the polyamine. Likewise, with a polyol having at least two reactive hydroxyl groups per molecule, the amount of succinic acylating agent used is generally such as to cause at least 1.6 succinic groups to react per molecule of the polyol.

Reaction temperatures used in forming the succinic derivatives of this invention are those sufficient to cause the desired reactions to occur. Generally speaking, the reactions are usually carried out at temperatures falling within the range of about 100 to about 250°C, and preferably in the range of about 140 to about 180°C. Water formed in the reaction is generally stripped from the reaction mixture during or after the reaction.

The succinic derivative compositions of this invention are either oil-soluble, or dissolvable in oil with the aid of a suitable solvent, or are oil-dispersible in the sense that they form stable dispersions in oil. Oil-soluble, dissolvable or oil-dispersible as that terminology is used herein does not necessarily indicate that the materials are soluble, dissolvable, miscible, or capable of being suspended in oil in all proportions. It does mean however that the additives are, for example, soluble or oil-dispersible to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit the incorporation of higher levels of a particular succinic derivative composition hereof, if desired.

The practice and advantages of this invention will become still further apparent from the following illustrative examples, which are not intended to limit, and should not be construed as limiting, the scope of this invention.

In these examples all parts and percentages are by weight unless otherwise specified. Also the "cook period" referred to in the examples is designated as the point where the reaction mass reaches its specified reaction temperature, and thus at this point the cook time is equal to 0. The polybutene used in Examples 1 and 2 was a substantially pure polyisobutylene with a number average molecular weight of about 995. Approximately 78% of the polymer

had an end group as depicted in Formula (Q) above. Conventional commercially-available polyisobutene contains less than about 10% of polymer containing such end group.

EXAMPLE 1

5 Into an autoclave were charged 1200 parts of polybutene (PIB),
130.7 parts of maleic anhydride (MA) and 0.12 part of aluminum tri-
chloride. The mole ratio of MA:PIB was thus 1:1. A vacuum (-26
inches of mercury) was applied to the autoclave for 10 minutes to
remove the oxygen (air), and while holding the system under a low
10 vacuum the autoclave was heated. When the autoclave temperature
reached 90°C, the agitator was turned on. When the temperature
reached 225°C, the pressure within the autoclave was 12.5 psig.
Thereupon the reaction mixture was kept at 225°C for 5 hours while
continuously agitating the reaction mixture. The pressure profile
15 on the reaction mass during this period was as follows:

	<u>Cook Time, minutes</u>	<u>Pressure, psig</u>
	0	12.5
	5	13.0
	15	8.0
20	25	5.0
	40	4.5
	50	3.5
	65	2.0
	80	1.0
25	95	0.5
	135	0
	150	-0.5
	170	0
	185	0.5
30	210	1.5
	235	3.0
	255	4.0
	300	6.0

The resultant reaction product was subjected to vacuum stripping to
35 remove volatiles (primarily unreacted maleic anhydride). The poly-
butenyl succinic anhydride reaction product had an acid number be-
fore stripping of 0.92, and an acid number after stripping of 0.76.

EXAMPLE 2

40 In this run the same reactants as in Example 1 were reacted at
240°C at a mole ratio (MA:PIB) of 1.1:1. The pressure profile on
the reaction mass during the reaction was as follows:

<u>Cook Time, minutes</u>	<u>Pressure, psig</u>
0	17.0

	10	15.0
	25	10.0
	30	9.0
	45	7.5
5	55	7.0
	65	6.0
	80	5.5
	95	6.0
	115	6.0
10	135	8.5
	155	10.0
	180	13.5
	195	16.0
	215	19.0
15	235	22.5
	250	25.5
	265	28.0
	280	31.5
	300	34.0

20 The reaction mixture before stripping had a total tar content of 3. The acid number of the polybutenyl succinic anhydride product after vacuum stripping was 0.91.

EXAMPLE 3

25 Polyisobutenylsuccinic anhydride (170 parts) formed as in Example 2 and pentaerythritol (68 parts) are reacted at 200 to 225°C for 4 hours in 200 parts of process oil. The reaction mixture is cooled to 160°C and 10 parts of tetraethylene pentamine (Dow S1107) is added and the reaction mixture maintained at 165°C for 1 hour.

30

EXAMPLE 4

The procedure of Example 3 is repeated substituting 60 parts of tris(hydroxymethyl)aminomethane for the tetraethylene pentamine.

EXAMPLE 5

35 In a first stage reaction, succinic ester-amide is produced as in Example 4. In a second stage reaction, maleic anhydride (MA) is added to the first stage reaction product in amount equivalent to 0.3 mole per mole of TEPA used in the first stage and the resultant mixture is heated at 165 to 170°C for 1.5 hours after which oil is added. In a third stage reaction, boric acid is added to the
40 second stage reaction mixture at a temperature of 150-155°C in an amount corresponding to 4.0 moles per 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 succic ester-amide is both acylated and boronated.

EXAMPLE 6

5 Polyisobutenylsuccinic anhydride formed as in Example 1 and tetraethylene pentamine (Dow S1107) in a mole ratio of 1.8:1 are reacted at 165-170°C for 4 hours.

EXAMPLE 7

The procedure of Example 6 is repeated substituting triethylene tetramine (Union Carbide) for the tetraethylene pentamine.

10

EXAMPLE 8

Polyisobutenylsuccinic anhydride formed as in Example 2 and tetraethylene pentamine (Dow S1107) in a mole ratio of 1.8:1 are reacted at 165°C for 2 hours.

EXAMPLE 9

15 The procedure of Example 8 is repeated substituting triethylene tetramine (Dow) for the tetraethylene pentamine.

EXAMPLE 10

The procedure of Example 8 is repeated substituting pentaethylene hexamine for the tetraethylene pentamine.

20

EXAMPLE 11

In a first stage reaction, polyisobutenylsuccinic anhydride (PIBSA) formed as in Example 2 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 0.3 moles per mole of TEPA used in the first stage and the resultant mixture is heated at 165-170°C for 1.5 hours. The succinimide is thus formed using a total mole ratio of anhydrides to TEPA of 2.1:1. To provide a handleable concentrate, the reaction product is suitably diluted with 100 solvent neutral mineral oil such that the nitrogen content of the blend is about 1.8%.

25

30

EXAMPLE 12

In a first stage reaction, PIBSA formed as in Example 2 and TEPA in a mole ratio of 2.05:1 are reacted at 165-170°C for 4 hours. In a second stage reaction, maleic acid is added to the first stage reaction product in amount equivalent to one mole per mole of TEPA used in the first stage and the resultant mixture is heated at 165-170°C for 1.5 hours. As in Example 11, the reaction product is suitably diluted with mineral oil base stock to provide a handleable concentrate.

40

EXAMPLE 13

The procedure of Example 12 is repeated except that fumaric acid is used in the second stage in amount equivalent to a mole ratio of 1:1 relative to the TEPA used in the first stage.

EXAMPLE 14

The procedure of Example 13 is repeated using an equivalent amount of malic acid in lieu of fumaric acid in the second stage.

EXAMPLE 15

5 The procedure of Example 14 is repeated using in the second stage an equivalent amount of succinic acid in lieu of malic acid.

EXAMPLE 16

10 A mixture is formed from 260 parts of a succinimide ashless dispersant formed as in Example 6, 100 parts of a 100 Solvent Neutral refined mineral oil diluent, 8 parts of phosphorous acid (H_3PO_3) in the form of solid flakes, 3.5 parts of tolutriazole, 8 parts of boric acid, and 3.0 parts of water. The mixture is heated at 100°C for two hours until all of the solid materials are dissolved. A vacuum of 40 mm Hg is gradually drawn on the product to
15 remove the water while the temperature is slowly raised to 110°C. A clear solution or composition is obtained which is soluble in oil.

EXAMPLE 17

20 The procedure of Example 16 is repeated except that dibutyl hydrogen phosphite (26 parts) and water (10 parts) are used in lieu of the phosphorous acid, and the amount of boric acid used is 10 parts.

EXAMPLE 18

25 The procedure of Example 17 is repeated except that the boric acid and water are omitted.

EXAMPLE 19

The procedure of Example 17 is repeated except that the phosphorous acid is omitted.

30 The succinimides, succinic esters, and succinic ester-amides, formed from the acylating agents described hereinabove can be subjected to a wide variety of subsequent reactions with post-treating agents. Typical post-treating agents, the conditions under which post-treatments are effected therewith, and typical improvements realized by such post-treatments are summarized below
35 in Table 3 with reference to prior disclosures dealing with post-treatment of succinimides, succinic esters, and/or succinic ester-amides formed from conventional acylating agents. Thus in the practice of this invention, the post-treating agents of the prior disclosures are used in the manner described therein with the
40 exception that in lieu of a conventional succinimide, succinic ester, and/or succinic ester-amide, a succinimide, succinic ester, and/or succinic ester-amide formed as in Published European Application No. 457,599 is used as the starting material for the post-treatment. In Table 3, all references to patent numbers are
45 to U.S. Patents except as otherwise specified.

Table 3 -- Post-Treatments

	Post-Treating Agents	Pat. Nos.
	Inorganic phosphorus acid or anhydride	3,403,102; 3,502,677; 3,513,093; 4,615,826; 4,648,980
5	Organic phosphorus compound	3,403,102; 3,502,677; 3,511,780; 3,513,093; GB 1,153,161 GB 2,140,811
	Phosphorus pentasulfide	3,184,411; 3,342,735
	Boron compound	3,087,936; 3,254,025; 3,281,428; 3,282,955; 2,284,409; 2,284,410; 3,338,832; 3,344,069; 3,533,945; 3,658,836; 3,703,536; 3,718,663; 4,455,243; 4,652,387;
	Mono- or polycarboxylic acid, anhydride, and/or acid halide	3,185,704; 3,216,936; 3,245,908; 3,245,909; 3,245,910; 3,415,750; 3,639,242; 3,692,681; 3,708,522; 4,548,724; 4,927,562; 4,948,386; GB 1,065,595; GB 1,162,436; GB 2,140,811; EP 0,438,849
10	Mono- or polyepoxide or thioepoxide	3,367,943; 3,373,111; 3,579,450; 3,859,318; 5,026,495; 5,030,369
	Aldehyde or ketone	3,369,021; 3,455,831; 3,455,832; 3,458,530;
	Carbon disulfide	3,200,107; 3,256,185

	Post-Treating Agents	Pat. Nos.
	Glycidol	4,617,137; 4,631,070
	Urea, thiourea or guanidine	3,312,619; 3,865,813; GB 1,065,595
	Organic sulfonic acid	3,189,544; GB 2,140,811
	Alkenyl cyanide	3,278,550; 3,366,569
5	Diketene	3,546,243
	A diisocyanate	3,573,205
	Alkane sultone	3,749,695
	1,3-Dicarbonyl compound	4,579,675
	Sulfate of alkoxylated alcohol or phenol	3,954,639
10	Cyclic lactone	4,617,138; 4,645,515; 4,668,246; 4,963,275; 4,971,711
	Cyclic carbonate or thiocarbonate, linear monocarbonate or polycarbonate, or chloroformate	4,612,132; 4,647,390; 4,648,886; 4,670,170
	Nitrogen-containing carboxylic acid	4,971,598; GB 2,140,811
15	Hydroxy-protected chlorodicarbonyloxy compound	4,614,522
	Lactam, thiolactam, thiolactone or dithiolactone	4,614,603; 4,666,460
	Cyclic carbamate, cyclic thiocarbamate or cyclic dithiocarbamate	4,663,062; 4,666,459
20	Hydroxyaliphatic carboxylic acid	4,482,464; 4,521,318; 4,713,189
	Oxidizing agent	4,379,064
	Combination of phosphorus pentasulfide and a polyalkylene polyamine	3,185,647
25	Combination of carboxylic acid or an aldehyde or ketone and sulfur or sulfur chloride	3,390,086; 3,470,098
	Combination of a hydrazine and carbon disulfide	3,519,564
	Combination of an aldehyde and a phenol	3,649,229; 5,030,249; 5,039,307
30	Combination of an aldehyde and an O,O-diester of dithiophosphoric acid	3,865,740
	Combination of a hydroxyaliphatic carboxylic acid and a boric acid	4,554,086

	Post-Treating Agents	Pat. Nos.
	Combination of a hydroxyaliphatic carboxylic acid, then formaldehyde and a phenol	4,636,322
	Combination of a hydroxyaliphatic carboxylic acid and then an aliphatic dicarboxylic acid	4,663,064
5	Combination of formaldehyde and a phenol, and then glycolic acid	4,699,724
	Combination of a hydroxyaliphatic carboxylic acid or oxalic acid and then a diisocyanate	4,713,191
10	Combination of inorganic acid or anhydride of phosphorus or a partial or total sulfur analog thereof and a boron compound	4,857,214
15	Combination of an organic diacid, then an unsaturated fatty acid, and then a nitroso-aromatic amine, optionally followed by a boron compound and then a glycolating agent	4,973,412
	Combination of an aldehyde and a triazole	4,963,278
	Combination of an aldehyde and a triazole, then a boron compound	4,981,492
20	Combination of cyclic lactone and a boron compound	4,963,275; 4,971,711

While this invention has been discussed with reference to use of polybutenes as the polyolefin reactant for producing the ashless dispersants of this invention, use can be made of other polyolefins having an end group configuration comparable to that depicted hereinabove, such as isopentene polymers, isohexene polymers, isobutene-propylene copolymers, isobutene-ethylene copolymers, isobutene-ethylene-propylene terpolymers, isobutene-amylene copolymers, and the like.

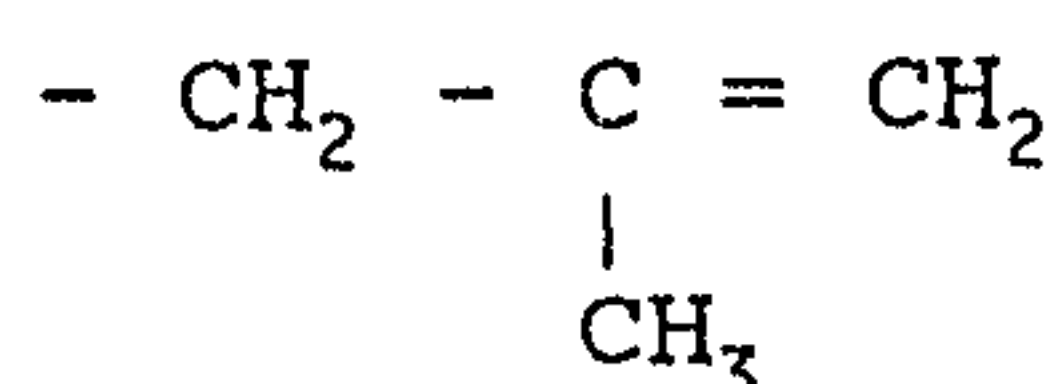
Also provided by this invention are compositions which comprise either at least one oil of lubricating viscosity or at least one liquid hydrocarbonaceous fuel and at least one succinic derivative composition of this invention. Such compositions include both additive concentrates or additive solutions and finished oleaginous compositions such as lubricants and functional fluids. Thus the proportions of the succinic derivative composition and the oil or fuel can vary widely depending upon the nature of the composition being formed. Thus in one of its embodiments this invention provides a carboxylic derivative composition in admixture with at least one oil of lubricating viscosity or at least one hydrocarbonaceous liquid fuel in weight proportions falling in the range of about 0.1 : 99.9 to about 99.9 : 0.1, and preferably in the range of about 0.5 : 99.5 to about 90 : 10, said carboxylic derivative composition being produced by reacting (a) at least one

substituted succinic acylating agent with (b) a combination of at least one amine having at least one primary or secondary amino group and at least one alcohol, the components of (b) being reacted with said at least one substituted succinic acylating agent concurrently or sequentially in any order, said at least one succinic acylating agent being prepared by reacting (i) at least one substantially aliphatic polymer of at least one lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula



wherein R and R' are independently -OH, -O-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process of preparing said at least one succinic acylating agent being characterized in that:

- a) the substantially aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the polyisobutene content of such polymer having an end group represented by the formula



- b) the mole ratio of said acidic reactant(s) : said polymer(s) is at least 1 : 1; and
- c) the reaction mixture is maintained under superatmospheric pressure during at least a substantial portion of the reaction period.

Preferred succinic derivative compositions for this use are formed from acylating agents of the type described above further characterized by having an average total tar rating as determined by the method described in the specification hereof that is at least about 40% lower, and most preferably at least 50% lower, than the average total tar rating of a corresponding product made in the same way under essentially the same reaction conditions using a polyisobutene containing less than 10% of the above-depicted end group. Particularly preferred succinic derivative compositions are those formed using acylating agents having a succination ratio of less than 1.3 -- i.e., the acylating agents have within their structure an average of less than 1.3 succinic groups per each substituent group derived from the aforesaid substantially aliphatic polymer.

The foregoing finished oleaginous compositions of this invention possess enhanced dispersant properties and thus are capable of being stored and used for long periods of time without excessive

formation and deposition of sludge and/or other similar deposits. Accordingly, the finished lubricant and functional fluid compositions can be used in a wide variety of applications such as engine oils, manual and automatic transmission fluids, gear oils, tractor
5 oils, cutting and machining oils, quenching oils, transformer oils, hydraulic fluids, general purpose lubricants, and the like. Similarly, the finished fuel compositions of this invention can be gasolines, diesel fuels, kerosene, home and/or industrial heating oils, burner fuels, gas oils, jet fuels, aviation fuels, gas turbine
10 fuels, bunker fuels, etc., depending upon the volatility and viscosity characteristics of the hydrocarbonaceous fuel itself. Compositions in which the hydrocarbonaceous fuel is a distillate fuel in the boiling range of about 150 to about 800°F are preferred.

15 In most cases, the finished lubricants and functional fluids of this invention will contain up to about 20% by weight of the succinic derivative composition, and in most cases the additive concentrates adapted for use in oils will contain up to about 80% by weight of one or more diluent oils of lubricating viscosity.
20 Similarly the finished hydrocarbonaceous fuels of this invention will contain up to about 10% by weight of the succinic derivative composition, and in most cases the additive concentrates adapted for use in oils will contain up to about 90% by weight of one or more inert diluents or carriers, such as a light petroleum fraction,
25 a light oil, a poly- α -olefin oligomer, a polyoxyalkylene glycol, a polyoxyalkylene monool, or the like.

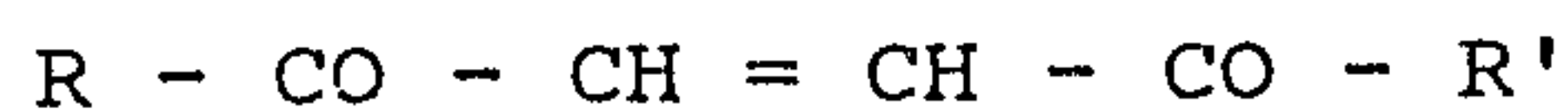
Further embodiments of the present invention are additive concentrates and lubricant or functional fluid compositions containing particular combinations of one or more additive components (hereinafter described) together with a carboxylic derivative composition
30 formed from a succinic acylating agent of the type described hereinabove (i.e., a succinimide, succinic ester, and/or a succinic ester-amide, such as are illustrated in the examples hereof). For convenience, these embodiments are referred to hereinbelow as
35 Embodiments A, B, C, and D.

Embodiment A

One such embodiment is an oil of lubricating viscosity or an additive concentrate for use in oil of lubricating viscosity containing at least the following components:

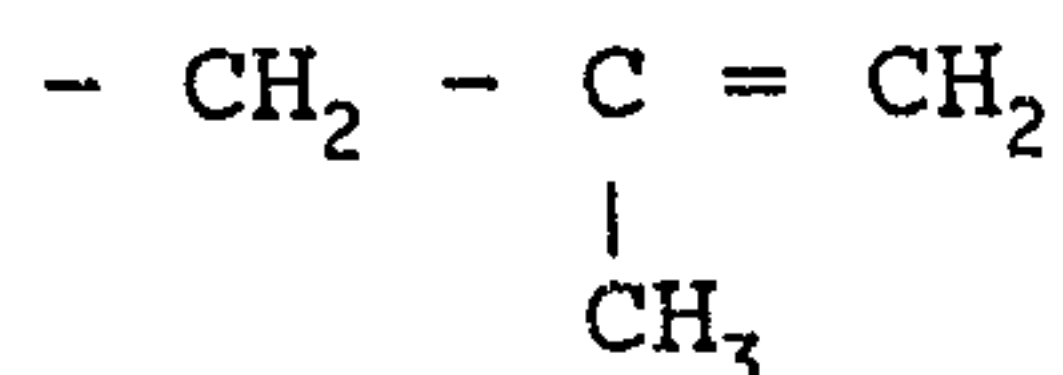
- 40 1) one or more oil-soluble zinc hydrocarbyl dithiophosphates; and
2) a carboxylic derivative composition produced by reacting at least one substituted succinic acylating agent with a reactant selected from the group consisting of (1) at least one amine

having at least one primary amino group, (2) at least one alcohol, and (3) a combination of at least one amine having at least one primary amino group and at least one alcohol, the components of (3) being reacted with said at least one substituted succinic acylating agent concurrently or sequentially in any order, said at least one succinic acylating agent being prepared by reacting (i) at least one substantially aliphatic polymer of at least one lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula



wherein R and R' are independently -OH, -O-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process of preparing said at least one succinic acylating agent being characterized in that:

- a) the substantially aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the polyisobutene content of such polymer having an end group represented by the formula



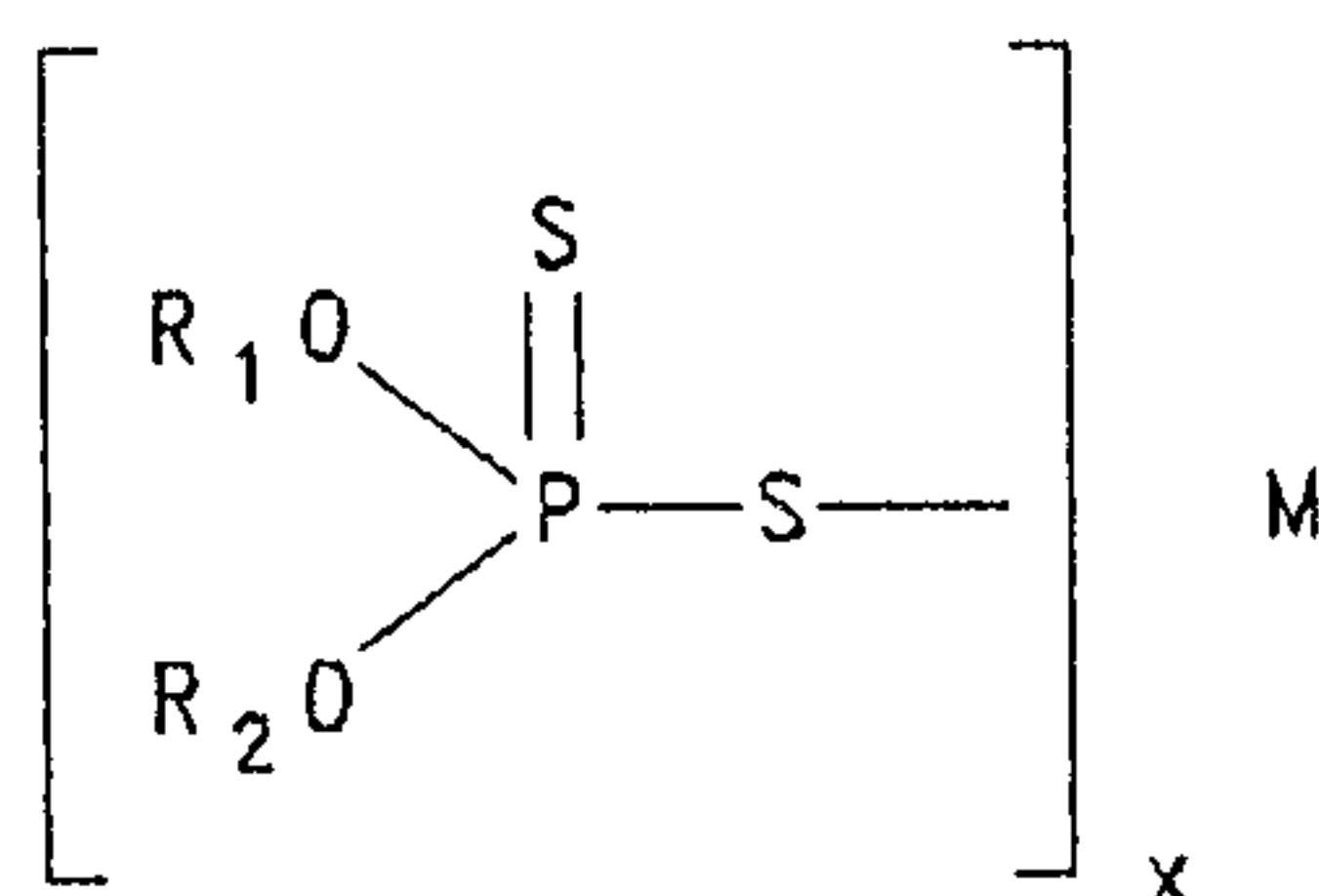
- b) the mole ratio of said acidic reactant(s) : said polymer(s) is at least 1 : 1; and
- c) the reaction mixture is maintained under superatmospheric pressure during at least a substantial portion of the reaction period.

Preferred carboxylic derivative compositions are formed using acylating agents as described above that are further characterized by having (i) an average total tar rating as determined by the method described in the specification hereof that is at least about 40% lower, and most preferably at least 50% lower, than the average total tar rating of a corresponding product made in the same way under essentially the same reaction conditions using a polyisobutene containing less than 10% of the above-depicted end group; and/or (ii) a succination ratio below 1.3.

The relative proportions of these components is preferably such that the weight ratio of phosphorus in 1) to nitrogen in 2) is in the range of from about 0.001:1 to about 100:1, and preferably in the range of about 0.01:1 to about 70:1. These combinations serve to inhibit wear; to inhibit deposit, varnish and/or sludge formation and/or deposition; and to protect the lubricant or functional fluid composition from premature oxidative degradation, es-

pecially at elevated temperatures. The quantity of these components 1) and 2) added to the base oil of lubricating viscosity (proportioned as described in this paragraph) is a minor dispersing amount, and is usually such that the amount of component 2) is in the range of about 0.01 to about 20% by weight of the total lubricating oil composition.

As is well known, zinc hydrocarbyl dithiophosphates are usually prepared by reacting phosphorus pentasulfide with one or more alcohols or phenolic compounds or diols to produce a hydrocarbyl dithiophosphoric acid which is then neutralized with one or more zinc-containing bases. When a monohydric alcohol or phenol is used in this reaction, the final product is a zinc dihydrocarbyl dithiophosphate. On the other hand, when a suitable diol (e.g., 2,4-pentanediol) is used in this reaction, the final product is a zinc salt of a cyclic hydrocarbyl dithiophosphoric acid. See, for example, U.S. Pat. No. 3,089,850. Thus typical oil-soluble zinc hydrocarbyl dithiophosphates used as component 1) may be represented by the formula



where R_1 and R_2 are, independently, hydrocarbyl groups or taken together are a single hydrocarbyl group forming a cyclic structure with the phosphorus and two oxygen atoms, preferably a hydrocarbyl-substituted trimethylene group of sufficient carbon content to render the compound oil soluble, M is zinc, and x is an integer corresponding to the valence of M. The preferred compounds are those in which R_1 and R_2 are separate hydrocarbyl groups (i.e., the zinc dihydrocarbyl dithiophosphates). Usually the hydrocarbyl groups of the zinc dihydrocarbyl dithiophosphates will contain no more than about 50 carbon atoms each although even higher molecular weight hydrocarbyl groups can be present in the compound. The hydrocarbyl groups include cyclic and acyclic groups, both saturated and unsaturated, such as alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, cycloalkylalkyl, aralkyl, and the like. It will be understood that the hydrocarbyl groups may contain elements other than carbon and hydrogen provided such other elements do not detract from the predominantly hydrocarbonaceous character of the hydrocarbyl group. Thus the hydrocarbyl groups may contain ether oxygen

atoms, thioether sulfur atoms, secondary or tertiary amino nitrogen atoms, and/or inert functional groups such as esterified carboxylic groups, keto groups, thioketo groups, and the like.

5 The phosphorodithioic acids from which the metal salts are formed can be prepared by the reaction of about 4 moles of one or more alcohols (cyclic or acyclic) or one or more phenols or mixture of one or more alcohols and one or more phenols (or about 2 moles of one or more diols) per mole of phosphorus pentasulfide, and the reaction may be carried out within a temperature range of from
10 about 50 to about 200°C. The reaction generally is completed in about 1 to 10 hours. Hydrogen sulfide is liberated during the reaction.

The alcohols used in forming the phosphorodithioic acids by the above method are preferably primary alcohols, or secondary al-
15 cohols. Mixtures thereof are also suitable. The primary alcohols include propanol, butanol, isobutyl alcohol, pentanol, 2-ethyl-1-hexanol, isooctyl alcohol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, octadecanol, eicosanol, and the like. The primary alcohols may contain various substituent groups such as
20 halogen atoms, nitro groups, etc., which do not interfere with the desired reaction. Among suitable secondary alcohols are included 2-butanol, 2-pentanol, 3-pentanol, 2-hexanol, 5-methyl-2-hexanol, and the like. In some cases, it is preferable to utilize mixtures of various alcohols, such as mixtures of 2-propanol with one or
25 more higher molecular weight primary alcohols, especially primary alcohols having from 4 to about 13 carbon atoms in the molecule. Such mixtures preferably contain at least 10 mole percent of 2-propanol, and usually will contain from about 20 to about 90 mole percent of 2-propanol. In one preferred embodiment, the alcohol
30 comprises about 30 to 50 mole percent of 2-propanol, about 30 to 50 mole percent isobutyl alcohol and about 10 to 30 mole percent of 2-ethyl-1-hexanol.

Other suitable mixtures of alcohols include 2-propanol/butanol; 2-propanol/2-butanol; 2-propanol/2-ethyl-1-hexanol; butanol/2-
35 ethyl-1-hexanol; isobutyl alcohol/2-ethyl-1-hexanol; and 2-propanol/tridecanol.

Cycloaliphatic alcohols suitable for use in the production of the phosphorodithioic acids include cyclopentanol, cyclohexanol, methylcyclohexanol, cyclooctanol, borneol and the like. Prefera-
40 bly, such alcohols are used in combination with one or more primary alkanols such as butanol, isobutyl alcohol, or the like.

5 Illustrative phenols which can be employed in forming the phosphorodithioic acids include phenol, o-cresol, m-cresol, p-cresol, 4-ethylphenol, 2,4-xyleneol, and the like. It is desirable to employ phenolic compounds in combination with primary alkanols such propanol, butanol, hexanol, or the like.

Other alcohols which can be employed include benzyl alcohol, cyclohexenol, and their ring-alkylated analogs.

10 It will be appreciated that when mixtures of two or more alcohols and/or phenols are employed in forming the phosphorodithioic acid, the resultant product will normally comprise a mixture of three or more different dihydrocarbyl phosphorodithioic acids, usually in the form of a statistical distribution in relation to the number and proportions of alcohols and/or phenols used.

15 Illustrative diols which can be used in forming the phosphorodithioic acids include 2,4-pentanediol, 2,4-hexanediol, 3,5-heptanediol, 7-methyl-2,4-octanediol, neopentyl glycol, 2-butyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, and the like.

20 The preparation of the zinc salts of the dihydrocarbyl dithiophosphoric acids or the cyclic hydrocarbyl dithiophosphoric acids is usually effected by reacting the acid product with a suitable zinc compound such as zinc oxide, zinc carbonate, zinc hydroxide, zinc alkoxide, or other appropriate zinc salt. Simply mixing and heating such reactants is normally sufficient to cause the reaction to occur and the resulting product is usually of sufficient purity
25 for use in the practice of this embodiment of the present invention. Typically, the salts are formed in the presence of a diluent such as an alcohol, water or a light mineral oil. Neutral salts are prepared by reacting one equivalent of the zinc oxide or hydroxide with one equivalent of the acid. Basic zinc salts are prepared by adding an excess (i.e., more than one equivalent) of the
30 zinc oxide or hydroxide with one equivalent of the dihydrocarbyl phosphorodithioic acid or cyclic hydrocarbyl phosphorodithioic acid.

35 In some cases, incorporation of certain ingredients such as small amounts of zinc acetate or acetic acid in conjunction with the zinc reactant will facilitate the reaction and provide an improved product. For example, use of up to about 5% of zinc acetate in combination with the required amount of zinc oxide tends to facilitate the formation of zinc dihydrocarbyl dithiophosphates.

Examples of useful zinc salts of dihydrocarbyl dithiophosphoric acids, and methods for preparing such salts are found in the prior art such as for example, U.S. Pat. Nos. 4,263,150; 4,289,635; 4,308,154; 4,322,479; 4,417,990; and 4,466,895.

5 Generally speaking, the preferred types of zinc salts of dihydrocarbyl dithiophosphoric acids are the oil-soluble zinc salts of dialkyl dithiophosphoric acids. Such compounds generally contain alkyl groups having at least three carbon atoms, and preferably the alkyl groups contain up to 10 carbon atoms although as noted above,
10 even higher molecular weight alkyl groups are entirely feasible. A few illustrative zinc dialkyl dithiophosphates include zinc diisopropyl dithiophosphate, zinc dibutyl dithiophosphate, zinc diisobutyl dithiophosphate, zinc di-sec-butyl dithiophosphate, the zinc dipentyl dithiophosphates, the zinc dihexyl dithiophosphates,
15 the zinc diheptyl dithiophosphates, the zinc dioctyl dithiophosphates, the zinc dinonyl dithiophosphates, the zinc didecyl dithiophosphates, and the higher homologs thereof. Mixtures of two or more such zinc compounds are often preferred for use, such as zinc salts of dithiophosphoric acids formed from mixtures of isopropyl
20 alcohol and secondary butyl alcohol; isopropyl alcohol, isobutyl alcohol, and 2-ethylhexyl alcohol; isopropyl alcohol, butyl alcohol, and pentyl alcohol; isobutyl alcohol and octyl alcohol; and the like.

Embodiment B)

25 Another embodiment of this invention is an oil of lubricating viscosity or an additive concentrate for use in oil of lubricating viscosity containing at least the following components:

- 1) one or more oil-soluble or oil-dispersible alkali or alkaline-earth metal-containing detergents; and
- 30 2) a carboxylic derivative composition produced by reacting at least one substituted succinic acylating agent with a reactant selected from the group consisting of (1) at least one amine having at least one primary amino group, (2) at least one alcohol, and (3) a combination of at least one amine having at
35 least one primary amino group and at least one alcohol, the components of (3) being reacted with said at least one substituted succinic acylating agent concurrently or sequentially in any order, said at least one succinic acylating agent being prepared by reacting (i) at least one substantially aliphatic
40 polymer of at least one lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula



wherein R and R' are independently -OH, -O-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process of preparing said at least one succinic acylating agent being characterized in that:

- 5 a) the substantially aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the polyisobutene content of such polymer having an end group represented by the formula



- b) the mole ratio of said acidic reactant(s) : said polymer(s) is at least 1 : 1; and
- 15 c) the reaction mixture is maintained under superatmospheric pressure during at least a substantial portion of the reaction period; and
- 3) optionally, one or more oil-soluble zinc hydrocarbyl dithiophosphates.

20 Preferred carboxylic derivative compositions are formed using acylating agents as described above that are further characterized by having (i) an average total tar rating as determined by the method described in the specification hereof that is at least about 40% lower, and most preferably at least 50% lower, than the average total tar rating of a corresponding product made in the same way

25 under essentially the same reaction conditions using a polyisobutene containing less than 10% of the above-depicted end group; and/or (ii) a succination ratio of less than 1.3.

30 It will be noted that in these compositions there are at least two required components, designated 1) and 2). This embodiment also includes a three-component mixture composed of the components designated as 1), 2) and 3). In these various combinations the relative proportions of these components is preferably such that the weight ratio of metal in 1) to nitrogen in 2) is in the range of from about 0.01:1 to about 1000:1, and preferably is in the

35 range of from about 0.1:1 to about 700:1, and such that when component 3) is employed, the weight ratio of phosphorus in component 3) to nitrogen in component 2) is in the range of from about 0.001:1 to about 100:1, and preferably in the range of about 0.01:1 to about 70:1. These combinations serve to inhibit wear; to inhibit deposit, varnish and/or sludge formation and/or deposition; and

40 to protect the lubricant or functional fluid composition from premature oxidative degradation, especially at elevated temperatures.

The quantity of these components 1) and 2), and optionally component 3) (proportioned as described in this paragraph) added to the base oil of lubricating viscosity is a minor dispersing amount, and is usually such that the amount of component 2) is in the range of about 0.01 to about 20% by weight of the total lubricating oil composition.

The metal-containing detergents which are employed in this embodiment are exemplified by oil-soluble or oil-dispersible basic salts of alkali or alkaline earth metals with one or more of the following acidic substances (or mixtures thereof): (1) sulfonic acids, (2) carboxylic acids, (3) salicylic acids, (4) alkylphenols, (5) sulfurized alkylphenols, (6) organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage. Such organic phosphorus acids include those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium. The salts for use in this embodiment are preferably basic salts having a TBN of at least 50, preferably above 100, and most preferably above 200. In this connection, TBN is determined in accordance with ASTM D-2896-88.

The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature of about 50°C, and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve* alcohol, Carbitol* alcohol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-betanaphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent and at least one alcohol

*Trade-mark

promoter, and carbonating the mixture at an elevated temperature such as 60° to 200°C.

5 Examples of suitable metal-containing detergents include, but are not limited to, the basic or overbased salts of such substances as lithium phenates, sodium phenates, potassium phenates, calcium phenates, magnesium phenates, sulfurized lithium phenates, sulfurized sodium phenates, sulfurized potassium phenates, sulfurized calcium phenates, and sulfurized magnesium phenates wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon
10 solubility; lithium sulfonates, sodium sulfonates, potassium sulfonates, calcium sulfonates, and magnesium sulfonates wherein each sulfonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility; lithium salicylates, sodium salicylates,
15 potassium salicylates, calcium salicylates, and magnesium salicylates wherein the aromatic moiety is usually substituted by one or more aliphatic substituents to impart hydrocarbon solubility; the lithium, sodium, potassium, calcium and magnesium salts of hydrolyzed phosphosulfurized olefins having 10 to 2,000 carbon atoms or
20 of hydrolyzed phosphosulfurized alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2,000 carbon atoms; lithium, sodium, potassium, calcium and magnesium salts of aliphatic carboxylic acids and aliphatic-substituted cycloaliphatic carboxylic acids; and many other similar alkali and alkaline earth metal salts
25 of oil-soluble organic acids. Mixtures of basic or overbased salts of two or more different alkali and/or alkaline earth metals can be used. Likewise, basic or overbased salts of mixtures of two or more different acids or two or more different types of acids (e.g., one or more calcium phenates with one or more calcium sulfonates)
30 can also be used. While rubidium, cesium and strontium salts are feasible, their expense renders them impractical for most uses. Likewise, while barium salts are effective, the status of barium as a heavy metal under a toxicological cloud renders barium salts less preferred for present-day usage.

35 As is well known, overbased metal detergents are generally regarded as containing overbasing quantities of inorganic bases, probably in the form of micro dispersions or colloidal suspensions. Thus the terms "oil-soluble" and "oil-dispersible" are applied to these metal-containing detergents so as to include metal detergents
40 wherein inorganic bases are present that are not necessarily completely or truly oil-soluble in the strict sense of the term, inasmuch as such detergents when mixed into base oils behave in much

the same way as if they were fully and totally dissolved in the oil.

Collectively, the various basic or overbased detergents referred to hereinabove, have sometimes been called, quite simply, basic alkali metal or alkaline earth metal-containing organic acid salts.

Methods for the production of oil-soluble basic and overbased alkali and alkaline earth metal-containing detergents are well known to those skilled in the art and are extensively reported in the patent literature. See for example, the disclosures of U.S. Pat. Nos. 2,451,345; 2,451,346; 2,485,861; 2,501,731; 2,501,732; 2,585,520; 2,671,758; 2,616,904; 2,616,905; 2,616,906; 2,616,911; 2,616,924; 2,616,925; 2,617,049; 2,695,910; 3,178,368; 3,367,867; 3,496,105; 3,629,109; 3,865,737; 3,907,691; 4,100,085; 4,129,589; 4,137,184; 4,148,740; 4,212,752; 4,617,135; 4,647,387; 4,880,550; GB Published Patent Application 2,082,619 A, and European Patent Publication Nos. 121,024 B1 and 259,974 A2.

Embodiment C

Still another embodiment of this invention is an oil of lubricating viscosity or an additive concentrate for use in oil of lubricating viscosity containing at least the following components:

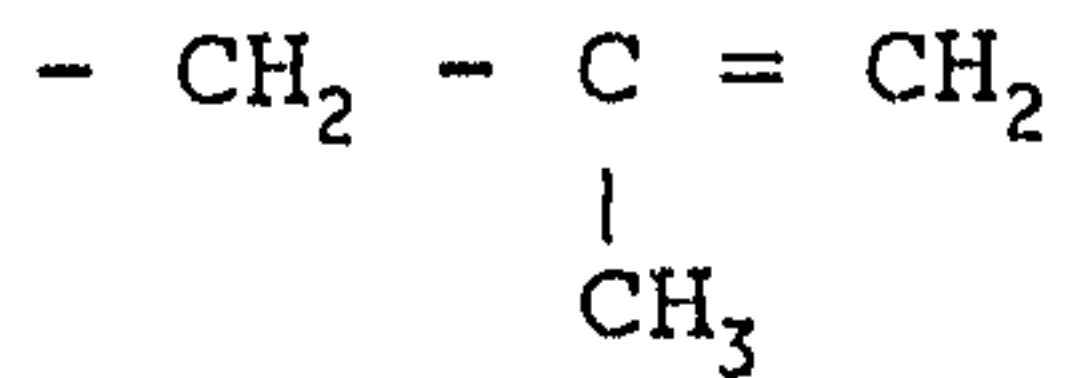
- 1) one or more oil-soluble or oil-dispersible sulfur-containing antiwear and/or extreme pressure agents; and
- 2) a carboxylic derivative composition produced by reacting at least one substituted succinic acylating agent with a reactant selected from the group consisting of (1) at least one amine having at least one primary amino group, (2) at least one alcohol, and (3) a combination of at least one amine having at least one primary amino group and at least one alcohol, the components of (3) being reacted with said at least one substituted succinic acylating agent concurrently or sequentially in any order, said at least one succinic acylating agent being prepared by reacting (i) at least one substantially aliphatic polymer of at least one lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula



wherein R and R' are independently -OH, -O-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process of preparing said at least one succinic acylating agent being characterized in that:

- a) the substantially aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the polyisobutene content of such polymer having an end group represented by the formula

5



- b) the mole ratio of said acidic reactant(s) : said polymer(s) is at least 1 : 1; and
- 10 c) the reaction mixture is maintained under superatmospheric pressure during at least a substantial portion of the reaction period; and
- 3) optionally, one or more oil-soluble zinc hydrocarbyl dithiophosphates; and/or
- 15 4) optionally, one or more oil-soluble or oil-dispersible alkali or alkaline earth metal detergents.

Preferred carboxylic derivative compositions are formed using acylating agents as described above that are further characterized by having (i) an average total tar rating as determined by the method described in the specification hereof that is at least about 40% lower, and most preferably at least 50% lower, than the average total tar rating of a corresponding product made in the same way under essentially the same reaction conditions using a polyisobutene containing less than 10% of the above-depicted end group; and/or (ii) a succination ratio below 1.3.

It will be noted that in these compositions there are at least two required components, designated 1) and 2). This embodiment also includes two three-component mixtures, the first composed of the components designated as 1), 2) and 3) and the second composed of the components designated as 1), 2) and 4). And additionally this embodiment comprises the four-component combinations composed of the components designated as 1), 2), 3) and 4). In these various combinations the relative proportions of these components is preferably such that the weight ratio of sulfur in 1) to nitrogen in 2) is in the range of from about 0.001:1 to about 100:1, and preferably in the range of about 0.01 to about 70:1; such that when component 3) is employed, the weight ratio of phosphorus as component 3) to nitrogen as component 2) is in the range of from about 0.001:1 to about 100:1, and preferably in the range of about 0.01:1 to about 70:1; and such that when component 4) is employed, the weight ratio of metal as component 4) to nitrogen as component 2) is in the range of from about 0.001:1 to about 1000:1, and prefer-

ably in the range of from about 0.1:1 to about 700:1. These combinations serve to inhibit wear; to inhibit deposit, varnish and/or sludge formation and/or deposition; and to protect the lubricant or functional fluid composition from premature oxidative degradation, especially at elevated temperatures. The quantity of these components 1) and 2), and optionally 3) and/or 4) (proportioned as described in this paragraph) added to the base oil of lubricating viscosity is a minor dispersing amount, and is usually such that the amount of component 2) is in the range of about 0.01 to about 20% by weight of the total lubricating oil composition.

Various types of sulfur-containing antiwear and/or extreme pressure agents can be used in the practice of Embodiment C. Examples are included within the categories of dihydrocarbyl polysulfides; sulfurized olefins; sulfurized fatty acid esters of both natural and synthetic origins; trithiones; sulfurized thienyl derivatives; sulfurized terpenes; sulfurized oligomers of C₂-C₈ monoolefins; and sulfurized Diels-Alder adducts such as those disclosed in U.S. reissue patent Re 27,331. Specific examples include sulfurized polyisobutene of Mn 1,100, sulfurized isobutylene, sulfurized diisobutylene, sulfurized triisobutylene, dicyclohexyl polysulfide, diphenyl polysulfide, dibenzyl polysulfide, dinonyl polysulfide, and mixtures of di-tert-butyl polysulfide such as mixtures of di-tert-butyl trisulfide, di-tert-butyl tetrasulfide and di-tert-butyl pentasulfide, among others. Combinations of such categories of sulfur-containing antiwear and/or extreme pressure agents can also be used, such as a combination of sulfurized isobutylene and di-tert-butyl trisulfide, a combination of sulfurized isobutylene and dinonyl trisulfide, a combination of sulfurized tall oil and dibenzyl polysulfide, and the like.

One type of sulfur-containing antiwear and/or extreme pressure agents is comprised of the oil-soluble active sulfur-containing antiwear and/or extreme pressure agents. Generally speaking, these are substances which possess a linkage of two or more sulfur atoms (e.g., -S-S-, -S-S-S-, -S-S-S-S-, S-S-S-S-S-, etc.).

To determine whether a sulfur-containing material is an active sulfur-containing material, use is made of a copper coupon corrosion test conducted as follows: A copper coupon approximately 70 x 15 mm and about 1.25 mm in thickness is cleaned by use of steel wool (0000 grade), washed with heptane, and then with acetone, dried, and weighed to the nearest 0.1 mg. The cleaned coupon is placed in a test tube and covered completely with the composition to be tested, and the system is heated to 125°C by means of an oil

bath. After holding the system at 125°C for three hours, the copper coupon is removed from the test tube, rinsed with heptane, and then with acetone. The dried coupon is then rubbed with a paper towel moistened with acetone to remove any surface flakes formed by copper corrosion. The coupon is then air-dried and weighed to the nearest 0.1 mg. The difference in weight between the initial copper coupon and the coupon after the test represents the extent to which the copper was corroded under the test conditions. Therefore the larger the weight difference, the greater the copper corrosion, and thus the more active the sulfur compound. If the coupon weight loss is 30 milligrams or more, the sulfur-containing agent is considered "active".

Another type of sulfur-containing antiwear and/or extreme pressure agents suitable for use in the practice of this invention is comprised of "non-active" sulfur-containing additives. These are materials which when subjected to the above copper coupon corrosion test give a weight loss of less than 30 milligrams. Examples of materials falling in this category include Anglamol* 33 additive (a sulfurized isobutylene product of The Lubrizol Corporation), distilled di-tert-butyl trisulfide, and the like.

Because of the toxicity of hydrogen sulfide, it is preferable, though not essential, to utilize in the practice of this invention oil-soluble sulfur-containing antiwear and/or extreme pressure agents, and more preferably oil-soluble active sulfur-containing antiwear and/or extreme pressure agents, that yield less than 25 ppm, and more preferably less than 10 ppm, of vapor space H₂S when heated in the concentrated state for one week at 65°C. Most preferred are materials of this type which yield no detectable vapor space H₂S when tested under these conditions.

The most preferred oil-soluble metal-free sulfur-containing antiwear and/or extreme pressure agents from the cost-effectiveness standpoint are the sulfurized olefins containing at least 30% by weight of sulfur, the dihydrocarbyl polysulfides containing at least 25% by weight of sulfur, and mixtures of such sulfurized olefins and polysulfides. Of these materials, sulfurized isobutylene having a sulfur content of at least 40% by weight and a chlorine content of less than 0.2% by weight is the most especially preferred material. Methods of preparing sulfurized olefins are described in U.S. Pat. Nos. 2,995,569; 3,673,090; 3,703,504; 3,703,505; 3,796,661; and 3,873,454. Also useful are the sulfurized olefin derivatives described in U.S. Pat. No. 4,654,156.

*Trade-mark

When including component 3) in the practice of Embodiment C, use can be made of any of the zinc hydrocarbyl dithiophosphates referred to hereinabove with reference to Embodiment A.

Embodiment D

5 A still further embodiment of this invention is an oil of lubricating viscosity or an additive concentrate for use in oil of lubricating viscosity containing at least the following components:

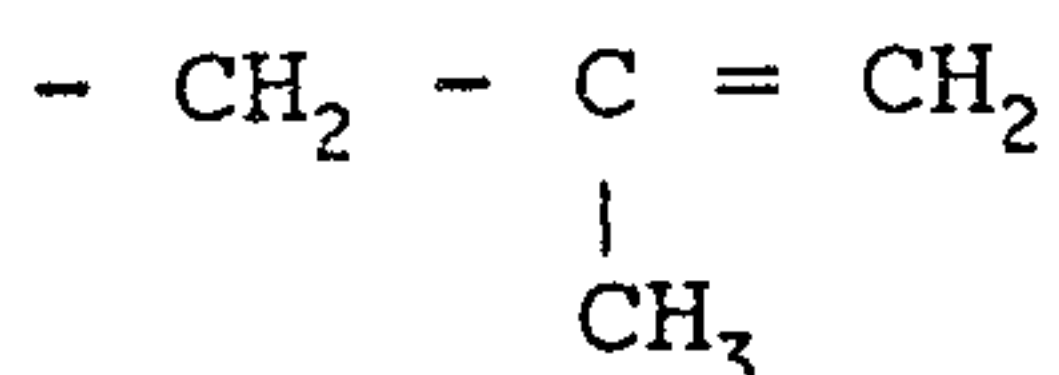
1) at least one oil-soluble metal-free phosphorus-containing (preferably phosphorus- and nitrogen-containing) antiwear
10 and/or extreme pressure agent, most preferably an amine salt of at least one dihydrocarbyl ester of a thiophosphoric acid; and

2) a carboxylic derivative composition produced by reacting at least one substituted succinic acylating agent with a reactant
15 selected from the group consisting of (1) at least one amine having at least one primary amino group, (2) at least one alcohol, and (3) a combination of at least one amine having at least one primary amino group and at least one alcohol, the components of (3) being reacted with said at least one substituted succinic acylating agent concurrently or sequentially
20 in any order, said at least one succinic acylating agent being prepared by reacting (i) at least one substantially aliphatic polymer of at least one lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula



wherein R and R' are independently -OH, -O-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process of preparing said at least one succinic acylating
30 agent being characterized in that:

a) the substantially aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the polyisobutene content of such polymer having an end group represented by the formula



b) the mole ratio of said acidic reactant(s) : said polymer(s) is at least 1 : 1; and

40 c) the reaction mixture is maintained under superatmospheric pressure during at least a substantial portion of the reaction period; and

- 3) optionally, one or more oil-soluble or oil-dispersible sulfur-containing antiwear and/or extreme pressure agents.

Preferred carboxylic derivative compositions of this embodiment are produced using acylating agents as described above that are further characterized by having (i) an average total tar rating as determined by the method described in the specification hereof that is at least about 40% lower, and most preferably at least 50% lower, than the average total tar rating of a corresponding product made in the same way under essentially the same reaction conditions using a polyisobutene containing less than 10% of the above-depicted end group; and/or (ii) a succination ratio below 1.3.

It will be noted that in these compositions there are at least two required components, designated 1) and 2). This embodiment also includes three-component mixtures composed of the components designated as 1), 2) and 3). In these various combinations the relative proportions of these components is preferably such that the weight ratio of phosphorus in 1) to nitrogen in 2) is in the range of from about 0.001:1 to about 100:1, and preferably in the range of about 0.01:1 to about 70:1; and such that when component 3) is employed, the weight ratio of sulfur in component 3) to nitrogen in component 2) is in the range of from about 0.001:1 to about 100:1, and preferably in the range of about 0.01 to about 70:1. These combinations serve to inhibit wear and to inhibit deposit, varnish and/or sludge formation and/or deposition. The quantity of these components 1) and 2), and optionally 3) (proportioned as described in this paragraph) added to the base oil of lubricating viscosity is a minor dispersing amount, and is usually such that the amount of component 2) is in the range of about 0.01 to about 20% by weight of the total lubricating oil composition.

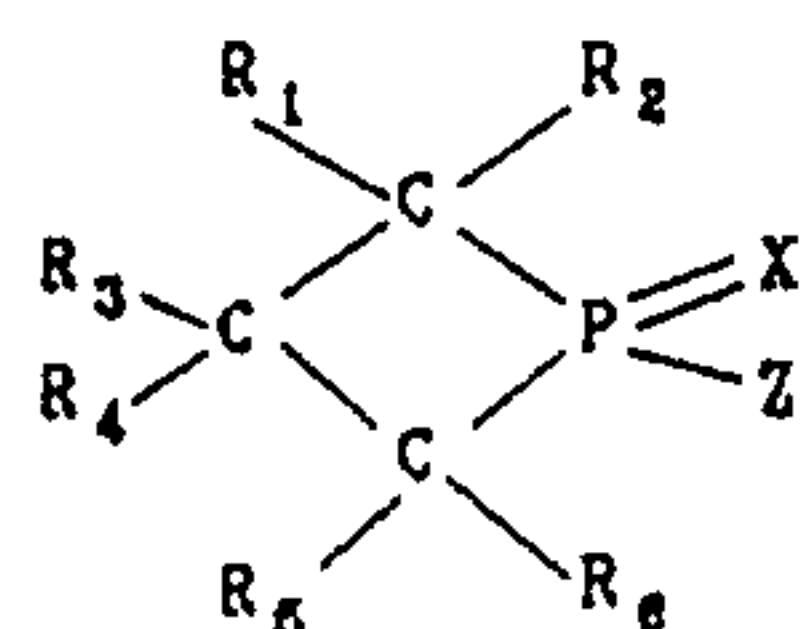
For purposes of this invention a component which contains both phosphorus and sulfur in its chemical structure is deemed a phosphorus-containing antiwear and/or extreme pressure agent rather than a sulfur-containing antiwear and/or extreme pressure agent.

Although use can be made of a wide variety of oil-soluble substances such as the oil-soluble organic phosphates, organic phosphites, organic phosphonates, organic phosphonites, etc., and their sulfur analogs, the preferred phosphorus-containing antiwear and/or extreme pressure agents for use in this embodiment those which contain both phosphorus and nitrogen.

Case EI-6086-A

One such type of phosphorus- and nitrogen-containing antiwear and/or extreme pressure additives which can be employed in the practice of this embodiment of the invention are the phosphorus- and nitrogen-containing compositions of the type described in G.B. 1,009,913; G.B. 1,009,914; U.S. 3,197,405 and/or U.S. 3,197,496. In general, these compositions are formed by forming an acidic intermediate by the reaction of a hydroxy-substituted triester of a phosphorothioic acid with an inorganic phosphorus acid, phosphorus oxide or phosphorus halide, and neutralizing a substantial portion of said acidic intermediate with an amine or hydroxy-substituted amine.

Another type of phosphorus- and nitrogen-containing antiwear and/or extreme pressure additive which can be used in the compositions of this invention is the amine salts of hydroxy-substituted phosphetanes or the amine salts of hydroxy-substituted thiophosphetanes. Typically, such salts are derived from compounds of the formula

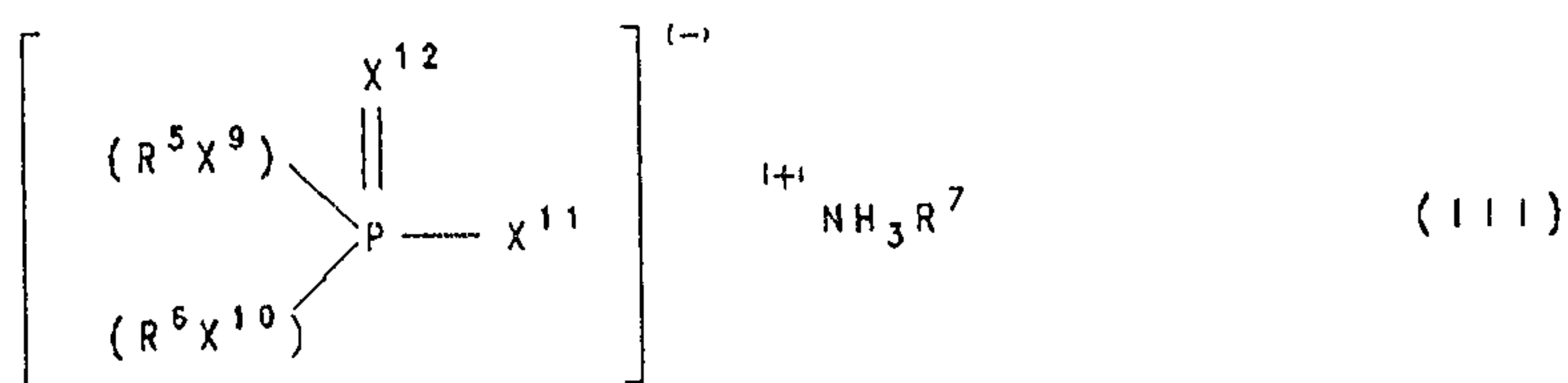
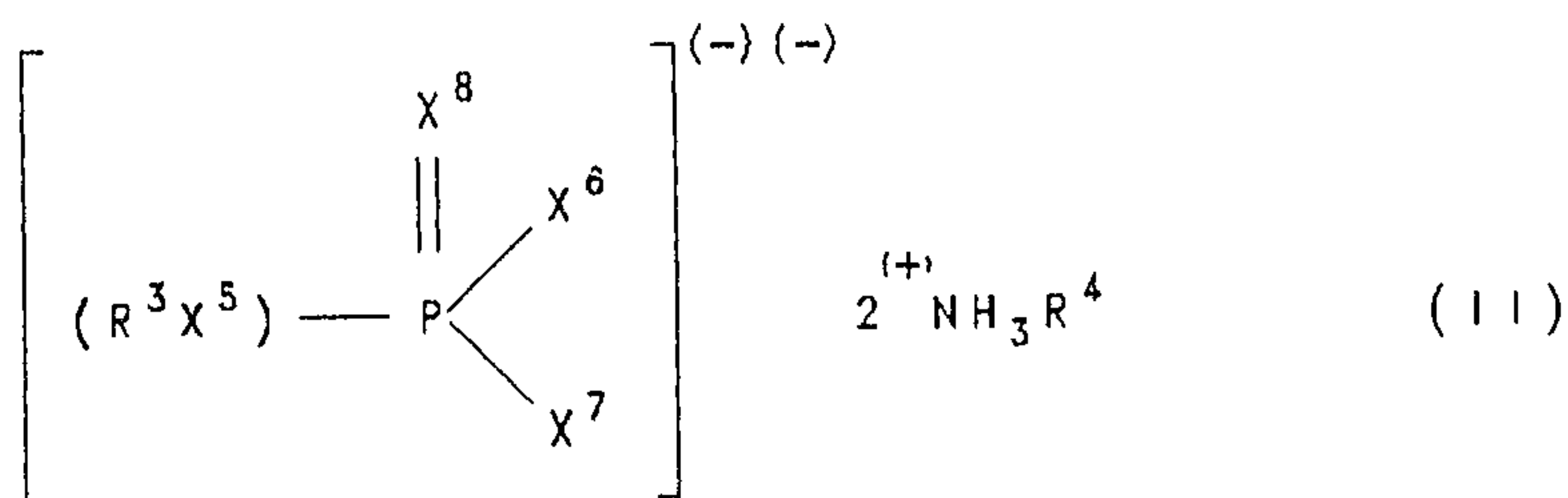
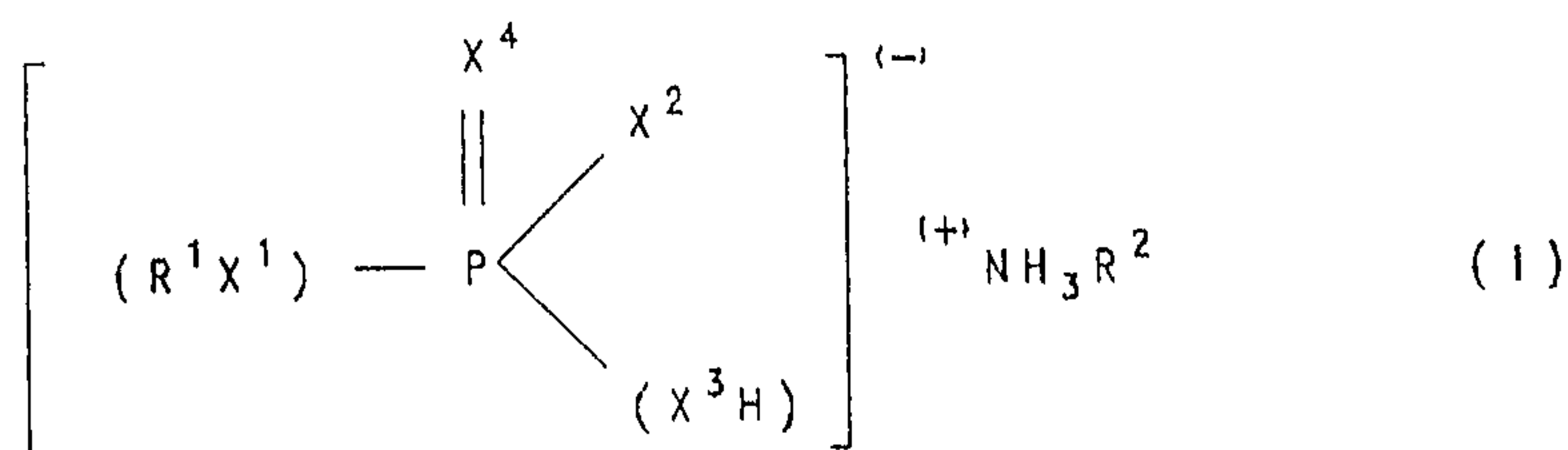


wherein each of R_1 , R_2 , R_3 , R_4 , R_5 and R_6 is a hydrogen atom or a carbon-bonded organic group such as a hydrocarbyl group or a substituted hydrocarbyl group wherein the substituent(s) do(es) not materially detract from the predominantly hydrocarbonaceous character of the hydrocarbyl group; X is a sulfur or an oxygen atom and Z is a hydroxyl group or an organic group having one or more acidic hydroxyl groups. Examples of this general type of antiwear and/or extreme pressure agent include the amine salts hydroxyphosphetanes and the amine salts of hydroxy-thiophosphetanes typified by Irgalube* 295 additive (Ciba-Geigy Corporation).

Another useful category of phosphorus- and nitrogen-containing antiwear and/or extreme pressure agents is comprised of the amine salts of partial esters of phosphoric and thiophosphoric acids.

*Trade-mark

Such compounds may be collectively represented by the formulas I, II, and III as follows:



5 or mixtures thereof. In Formulas I, II and III, each of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , and R^7 is, independently, a hydrocarbyl group and each of X^1 , X^2 , X^3 , X^4 , X^5 , X^6 , X^7 , X^8 , X^9 , X^{10} , X^{11} , and X^{12} is, independently, an oxygen atom or a sulfur atom.

10 In one preferred sub-category the amine salts are formed with one or more partially esterified monothiophosphoric acids. These are compounds of Formulas I, II, and III above wherein only one of X^1 , X^2 , X^3 , and X^4 , only one of X^5 , X^6 , X^7 , and X^8 , and only one of X^9 , X^{10} , X^{11} , and X^{12} is a sulfur atom.

15 In another preferred sub-category the amine salts are formed with one or more partially esterified phosphoric acids. These are compounds of Formulas I, II, and III above wherein all of X^1 , X^2 , X^3 , X^4 , X^5 , X^6 , X^7 , X^8 , X^9 , X^{10} , X^{11} , and X^{12} are oxygen atoms.

Another preferred sub-category of amine salts are those formed with one or more partially esterified dithiophosphoric acids. These are compounds of Formulas I, II, and III above wherein two of X^1 , X^2 , X^3 , and X^4 , two of X^5 , X^6 , X^7 , and X^8 , and two of X^9 , X^{10} , X^{11} , and X^{12} are sulfur atoms.

Also useful are amine salts of Formulas I, II, and III above wherein three or four of X^1 , X^2 , X^3 , and X^4 , three or four of X^5 , X^6 , X^7 , and X^8 , and three or four of X^9 , X^{10} , X^{11} , and X^{12} are sulfur atoms.

While all of the above oil-soluble amine salts are suitable for use as component 3), it is most preferred to use at least one oil-soluble amine salt of a dihydrocarbyl monothiophosphoric acid (one sulfur atom per molecule), either alone or in combination with at least one oil-soluble amine salt of a dihydrocarbyl phosphoric acid (no sulfur atom in the molecule).

Suitable salts or amine adducts include: octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, cyclohexylamine, phenylamine, mesitylamine, oleylamine, cocoamine, soyamine, C_8 tertiary alkyl primary amine, C_{12-14} tertiary alkyl primary amine, C_{22-24} tertiary alkyl primary amine, phenethylamine, etc., salts or adducts of partially esterified phosphoric, monothiophosphoric, dithiophosphoric, trithiophosphoric, and/or tetrathiophosphoric acids, including mixtures of any such compounds. Generally speaking, the preferred amine salts are salts of aliphatic amines, especially the saturated or olefinically unsaturated aliphatic primary amines, such as n-octylamine, 2-ethylhexylamine, tert-octylamine, n-decylamine, the C_{10} , C_{12} , C_{14} and C_{16} tertiary alkyl primary amines (either singly or in any combinations thereof, such as a mixture of the C_{12} and C_{14} tertiary alkyl primary amines), n-undecylamine, a mixture of C_{14} to C_{18} tertiary alkyl primary amines, lauryl amine, hexadecylamine, heptadecylamine, octadecylamine, the C_{22} and C_{24} tertiary alkyl primary amines (either singly or in combination), decenylamine, dodecenylamine, palmitoleylamine, oleylamine, linoleylamine, eicosenylamine, etc. Secondary hydrocarbyl amines and tertiary hydrocarbyl amines can also be used either alone or in combination with each other or in combination with primary amines. Thus any combination of primary, secondary and/or tertiary amines, whether monoamine or polyamine, can be used in forming the salts or adducts.

Similarly, the amines used can be in the form of polyalkylene polyamines; functionally-substituted polyamines such as a succinimide or succinamide of a polyalkylene polyamines such as a polyisobutenyl succinimide of diethylene triamine, a polyisobutenyl succinimide of triethylene tetramine, a polyisobutenyl succinimide of tetraethylene pentamine, a polyisobutenyl succinimide of pentaethylene hexamine (including succinimides made from commercially available polyethylene polyamine mixtures which contain linear, branched and cyclic species); and Mannich bases derived from polyalkylene polyamines of the types just described. Moreover, the polyalkylene polyamines whether in the free state or in the form of a succinimide, succinamide, or Mannich base, can be partially boronated, partially phosphorylated, or partially acylated with a reagent such as maleic anhydride, malic acid, itaconic acid, itaconic anhydride, thiomalic acid, fumaric acid, and the like, provided that such boronated or phosphorylated or acylated amine or amine moiety contains at least sufficient residual basicity to enable it to form a salt with the partially esterified phosphoric or thiophosphoric acid. Alkylene polyamines in the form of succinimides, succinamides or Mannich bases which have been boronated and phosphorylated are described for example in U.S. Pat. No. 4,857,214.

Use of primary amines is preferred. Especially preferred amines are alkyl monoamines and alkenyl monoamines having from about 8 to about 24 carbon atoms in the molecule.

Amines having less than 8 carbon atoms can be used, including methyl amine, etc., provided the resultant amine salt is oil-soluble. Likewise, amines having more than 24 carbon atoms can be used, again with the proviso that the resultant amine salt is oil soluble.

Methods for the preparation of such amine salts are well known and reported in the literature. See for example, U.S. Pat. Nos. 2,063,629; 2,224,695; 2,447,288; 2,616,905; 3,984,448; 4,431,552; Pesin et al, Zhurnal Obshchei Khimii, Vol. 31, No. 8, pp. 2508-2515 (1961); and International Application Publication No. WO 87/07638.

It should be noted that amine salts of partially esterified monothiophosphoric acids are usually made by reacting a mono- and/or dihydrocarbyl phosphite with sulfur or an active sulfur-containing compound such as are referred to above under the caption "Sulfur-Containing Antiwear and/or Extreme Pressure Agents" and one or more primary or secondary amines. Such reactions tend to be

highly exothermic reactions which can become uncontrollable, if not conducted properly. One preferred method of forming these amine salts involves a process which comprises (i) introducing, at a rate such that the temperature does not exceed about 60°C, one or more dihydrocarbyl hydrogen phosphites, such as a dialkyl hydrogen phosphite, into an excess quantity of one or more active sulfur-containing materials, such as sulfurized branched-chain olefin (e.g., isobutylene, diisobutylene, triisobutylene, etc.), while agitating the mixture so formed, (ii) introducing into this mixture, at a rate such that the temperature does not exceed about 60°C, one or more aliphatic primary or secondary amines, preferably one or more aliphatic primary monoamines having in the range of about 8 to about 24 carbon atoms per molecule while agitating the mixture so formed, and (iii) maintaining the temperature of the resultant agitated reaction mixture at between about 55 and about 60°C until reaction is substantially complete. Another suitable way of producing these amine salts is to concurrently introduce all three of the reactants into the reaction zone at suitable rates and under temperature control such that the temperature does not exceed about 60°C. Another preferred way of forming amine salts of partially esterified monothiophosphoric acids is to pre-react elemental sulfur with the amine for a short period of time and then add thereto the appropriate dihydrocarbyl hydrogen phosphite at a rate such that the temperature does not become excessive and the reaction uncontrollable.

As indicated above, the amine salts of dihydrocarbyl esters of thiophosphoric acids are comprised of the oil-soluble amine salts (preferably the aliphatic monoamine salts) of one or more dihydrocarbyl esters of a thiophosphoric acid, which esters can be derived from a tetrathiophosphoric acid, a trithiophosphoric acid, a dithiophosphoric acid, or a monothiophosphoric acid, or a mixture of any two or more of the foregoing. The amine salts of dihydrocarbyl esters of a dithiophosphoric acid are preferred, and the amine salts of dihydrocarbyl esters of a monothiophosphoric acid are particularly preferred.

As pointed out above, oil-soluble phosphorus- and nitrogen-containing compounds are the preferred antiwear and/or extreme pressure agents for use in the compositions of this invention. However, metal-free phosphorus-containing compounds which do not contain nitrogen can be used either in lieu of or in addition to the phosphorus- and nitrogen-containing antiwear and/or extreme pressure agents described above. Such nitrogen-free compounds are for the most part partially or fully esterified acids of phospho-

rus, and include for example oil-soluble phosphates, phosphites, phosphonates, phosphonites, and their various sulfur analogs. Examples include monohydrocarbyl phosphites; monohydrocarbyl phosphates; monohydrocarbyl mono-, di-, and trithiophosphites; mono-
5 hydrocarbyl mono-, di-, tri-, and tetrathiophosphates; dihydrocarbyl phosphites; dihydrocarbyl phosphates; dihydrocarbyl mono-, di-, and trithiophosphites; dihydrocarbyl mono-, di-, tri-, and tetrathiophosphates; trihydrocarbyl phosphites; trihydrocarbyl phosphates; trihydrocarbyl mono-, di-, and trithiophosphites; trihydrocarbyl mono-, di-, tri-, and tetrathiophosphates; the various hydrocarbyl phosphonates and thiophosphonates; the various hydrocarbyl phosphonites and thiophosphonites, and analogous oil-soluble derivatives of polyphosphoric and polythiophosphoric acids; and many others. A few specific examples of such compounds are tri-
15 butyl phosphate, tri-(2-ethylhexyl) phosphate, trioleyl phosphate, tris(2-chloroethyl) phosphate, tricyclohexyl phosphate, triphenyl phosphate, tricresyl phosphate, cresyl diphenyl phosphate, triethyl phosphite, tributyl phosphite, tris(2-butoxyethyl) phosphite, trioctyl phosphite, tris(tridecyl) phosphite, trilauryl phosphite, triphenyl phosphite, tricresyl phosphite, the mono- or diamyl hydrogen phosphates or mixtures thereof, the mono- or di-2-ethyl-1-hexyl hydrogen phosphates or mixtures thereof, dibutyl hydrogen phosphite, bis(tridecyl) hydrogen phosphite, the diisooctyl ester of butylphosphonic acid, the dihexyl ester of decylphosphonic acid,
20 sulfur-containing analogs of each of the foregoing, dihexyl thiophosphite, diisopropyl dithiophosphate, tris(tridecyl)tetrathiophosphate, and like compounds. Also useful are the oil-soluble heterocyclic phosphorus compounds such as the phosphetanes and thiophosphetanes and their derivatives, such as are described for example in U.S. Pat. Nos. 3,891,726; 3,975,465; Journal of The Chemical Society, Dalton Transactions, 1973, pages 1576-1582; 2641-2646; 2701-2707; and Ibid, 1974, pages 633-638.

When including component 3) in the practice of Embodiment D, use can be made of any of the oil-soluble and/or oil-dispersible
35 sulfur-containing antiwear and/or extreme pressure agents referred to hereinabove with reference to Embodiment C.

The lubricating oil compositions and additive concentrates of this invention, including the compositions of Embodiments A), B), C), and D) can, and in most cases will, contain still additional
40 components, such as one or more of the following:
Amine salts of carboxylic acids, demulsifiers, copper corrosion inhibitors, supplemental ashless dispersants, antioxidants,

rust inhibitors, antifoam agents, friction modifiers, seal swell agents, viscosity index improvers, pour point depressants, other metal corrosion inhibitors, and the like. For further details, reference should be had to U.S. Pat. No. 5,137,980.

5 These various types of other additives which can be used in the compositions of this invention is not to be construed as limitative, as many other types of additives can be used in such compositions. The only requirements are that such other additives not
10 excessively interfere adversely with the performance of the compositions of this invention and that they exhibit suitable compatibility with the additives otherwise being employed therein.
 Base oils.

 The ashless dispersants of this invention and the additive combinations of this invention can be incorporated in a wide variety
15 of lubricants and functional fluids in effective amounts to provide suitable active ingredient concentrations. The base oils not only can be hydrocarbon oils of lubricating viscosity derived from petroleum (or tar sands, coal, shale, etc.), but also can be natural oils of suitable viscosities such as rapeseed oil, etc.,
20 and synthetic 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; fluo-
25 rohydrocarbon oils; and mixtures of mineral, natural and/or synthetic oils in any proportion, etc. The term "base oil" for this disclosure includes all the foregoing.

 The additive combinations of this invention can thus be used in lubricating oil and functional fluid compositions, such as auto-
30 motive crankcase lubricating oils, automatic transmission fluids, gear oils, hydraulic oils, cutting oils, etc., in which the base oil of lubricating viscosity is 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.

35 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. Among the general types of petroleum oils
40 useful in the compositions of this invention are solvent neutrals, bright stocks, cylinder stocks, residual oils, hydrocracked base stocks, paraffin oils including pale oils, and solvent extracted naphthenic oils. Such oils and blends of them are produced by a

number of conventional techniques which are widely known by those skilled in the art.

As is noted above, the base oil can consist essentially of or comprise a portion of one or more synthetic oils. Among the suitable synthetic oils are homo- and inter-polymers of C_2 - C_{12} olefins, carboxylic acid esters of both monoalcohols and polyols, polyethers, silicones, polyglycols, silicates, alkylated aromatics, carbonates, thiocarbonates, orthoformates, phosphates and phosphites, borates and halogenated hydrocarbons. Representative of such oils are homo- and interpolymers of C_2 - C_{12} monoolefinic hydrocarbons, alkylated benzenes (e.g., dodecyl benzenes, didodecyl benzenes, tetradecyl benzenes, dinonyl benzenes, di-(2-ethylhexyl)benzenes, wax-alkylated naphthalenes); and polyphenyls (e.g., biphenyls, terphenyls). Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of synthetic oils. These are exemplified by the oils prepared through polymerization of alkylene oxides such as ethylene oxide or propylene oxide, and the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl polyisopropylene glycol ether having an average molecular weight of 1,000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1,000, diethyl ether of polypropylene glycol having a molecular weight of 1,000-1,500) or mono- and poly-carboxylic esters thereof, for example, the acetic acid ester, mixed C_3 - C_6 fatty acid esters, or the C_{13} Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) adipate, didodecyl adipate, di(tridecyl) adipate, di(2-ethylhexyl) sebacate, dilauryl sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, di(eicosyl) sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Other esters which may be used include those made from C_3 - C_{18} monocarboxylic acids and polyols and polyol ethers such as neopen-

5 tyl glycol, trimethylolpropane, pentaerythritol and dipentaerythritol. Trimethylol propane tripelargonate, pentaerythritol tetracaproate, the ester formed from trimethylolpropane, caprylic acid and sebacic acid, and the polyesters derived from a C_4 - C_{14} dicarboxylic acid and one or more aliphatic dihydric C_3 - C_{12} alcohols such as derived from azelaic acid or sebacic acid and 2,2,4-trimethyl-1,6-hexanediol serve as examples.

10 Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, poly(methyl)siloxanes, and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, triphenyl phosphite, and diethyl ester of decane phosphonic acid.

20 Also useful as base oils or as components of base oils are hydrogenated or unhydrogenated liquid oligomers of C_6 - C_{16} α -olefins, such as hydrogenated or unhydrogenated oligomers formed from 1-decene. Methods for the production of such liquid oligomeric 1-alkene hydrocarbons are known and reported in the literature. See for example U. S. Pat. Nos. 3,749,560; 3,763,244; 3,780,128; 4,172,855; 4,218,330; 4,902,846; 4,906,798; 4,910,355; 4,911,758; 4,935,570; 4,950,822; 4,956,513; and 4,981,578. Additionally, hydrogenated 1-alkene oligomers of this type are available as articles of commerce, e.g., under the trade designations ETHYLFLO 162, ETHYLFLO 164, ETHYLFLO 166, ETHYLFLO 168, ETHYLFLO 170, ETHYLFLO 174, and ETHYLFLO 180 poly- α -olefin oils (Ethyl Corporation; Ethyl Canada Limited; Ethyl S.A.). ETHYLFLO is a trademark of Ethyl Corporation. Blends of such materials can also be used in order to adjust the viscometrics of the given base oil. Suitable 1-alkene oligomers are also available from other suppliers. As is well known, hydrogenated oligomers of this type contain little, if any, residual ethylenic unsaturation.

35 Preferred oligomers are formed by use of a Friedel-Crafts catalyst (especially boron trifluoride promoted with water or a C_{1-20} alkanol) followed by catalytic hydrogenation of the oligomer so formed using procedures such as are described in the foregoing U.S. patents.

40 Other catalyst systems which can be used to form oligomers of 1-alkene hydrocarbons, which, on hydrogenation, provide suitable

oleaginous liquids include Ziegler catalysts such as ethyl aluminum sesquichloride with titanium tetrachloride, aluminum alkyl catalysts, chromium oxide catalysts on silica or alumina supports and a system in which a boron trifluoride catalyst oligomerization is followed by treatment with an organic peroxide.

It is also possible in accordance with this invention to utilize blends of one or more liquid hydrogenated 1-alkene oligomers in combination with other oleaginous materials having suitable viscosities, provided that the resultant blend has suitable compatibility and possesses the physical properties desired.

For some applications, for example use under conditions where oxidative or thermal degradation of the base oil is unlikely to be experienced, unhydrogenated 1-alkene oligomers can be used as the base oil or as a component in a base oil blend.

Likewise, various proprietary synthetic lubricants such as KETJENLUBE^{*} synthetic oil of Akzo Chemicals can be employed either as the sole base lubricant or as a component of the base lubricating oil.

Typical natural oils that may be used as base oils or as components of the base oils 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, meadowfoam oil, and the like. Such oils may be partially or fully hydrogenated, if desired.

The fact that the base oils used in the compositions of this invention may be composed of (i) one or more mineral oils, (ii) one or more synthetic oils, (iii) one or more natural oils, or (iv) a blend of (i) and (ii), or (i) and (iii), or (ii) and (iii), or (i), (ii) and (iii) does not mean that these various types of oils are necessarily equivalents of each other. Certain types of base oils may be used in certain compositions for the specific properties they possess such as biodegradability, high temperature stability, non-flammability or lack of corrosivity towards specific metals (e.g. silver or cadmium). In other compositions, other types of base oils may be preferred for reasons of availability or low cost. Thus, the skilled artisan will recognize that while the various types of base oils discussed above may be used in the compositions of this invention, they are not necessarily functional equivalents of each other in every instance.

^{*}Trade-mark

Proportions and Concentrations

In general, the components of the additive compositions of this invention are employed in the oleaginous liquids (e.g., lubricating oils and functional fluids) in minor amounts sufficient to improve the performance characteristics and properties of the base oil or fluid. The amounts of the components used in the base oil will vary in accordance with such factors as the viscosity characteristics of the base oil or fluid employed, the viscosity characteristics desired in the finished product, the service conditions for which the finished product is intended, and the performance characteristics desired in the finished product. However, generally speaking, the amounts of the components utilized in Embodiments A, B, C and D will fall in the ranges set forth hereinabove. The following concentrations (weight percent) of other components (on an active ingredients basis, i.e., excluding diluents which often are associated therewith) in the base oils or fluids are illustrative:

	Typical Range	Preferred Range
Amine salt of carboxylic acid	0 - 1	0.01 - 2
Demulsifier	0 - 0.5	0 - 0.2
Cu corrosion inhibitor	0 - 0.5	0.01 - 0.2
Supplemental ashless dispersant	0 - 3	0 - 2
Antioxidant	0 - 2	0 - 1
Rust inhibitor	0 - 1	0.02 - 0.5
Antifoam agent	0 - 0.3	0.0002 - 0.1
Friction modifier	0 - 2	0 - 1
Seal swell agent	0 - 20	0 - 10
Viscosity index improver	0 - 20	0 - 15
Pour point depressant	0 - 2	0 - 1
Other metal corrosion inhibitors	0 - 1	0 - 0.5

It is to be noted that some additives are multifunctional additives capable of contributing more than a single property to the blend in which they are used. Thus when employing a multifunctional additive component in the compositions of this invention, the amount used should of course be sufficient to achieve the function(s) and result(s) desired therefrom.

It will be appreciated that the individual components can be separately blended into the base oil or fluid or can be blended therein in various subcombinations, if desired. Moreover, such components can be blended in the form of separate solutions in a diluent. Except for viscosity index improvers and/or pour point

depressants (which in many instances are blended apart from other components), it is preferable to blend the other selected components into the base oil by use of an additive concentrate of this invention, as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate.

The additive concentrates of this invention will contain the individual components in amounts proportioned to yield finished oil or fluid blends consistent with the concentrations tabulated above. In most cases, the additive concentrate will contain one or more diluents such as light mineral oils, to facilitate handling and blending of the concentrate. Thus concentrates containing up to 80% by weight of one or more diluents or solvents can be used.

The oleaginous liquids provided by this invention can be used in a variety of applications. For example, they can be employed as crankcase lubricants, gear oils, hydraulic fluids, manual transmission fluids, automatic transmission fluids, cutting and machining fluids, brake fluids, shock absorber fluids, heat transfer fluids, quenching oils, transformer oils, and the like. The compositions are particularly suitable for use as automotive and industrial gear oils.

Blending

The formulation or blending operations are relatively simple and involve mixing together in a suitable container or vessel, using a dry, inert atmosphere where necessary or desirable, appropriate proportions of the selected ingredients. Those skilled in the art are cognizant of and familiar with the procedures suitable for formulating and blending additive concentrates and lubricant compositions. Usually the order of addition of components to the blending tank or vessel is not critical provided of course, that the components being blended at any given time are not incompatible or excessively reactive with each other. Agitation such as with mechanical stirring equipment is desirable to facilitate the blending operation. Frequently it is helpful to apply sufficient heat to the blending vessel during or after the introduction of the ingredients thereto, so as to maintain the temperature at, say, 40-60°C, and preferably no higher than about 60°C. Similarly, it is sometimes helpful to preheat highly viscous components to a suitable temperature even before they are introduced into the blending vessel in order to render them more fluid and thereby facilitate their introduction into the blending vessel and render the resultant mix-

ture easier to stir or blend. Naturally the temperatures used during the blending operations should be controlled so as not to cause any significant amount of thermal degradation or unwanted chemical interactions.

- 5 When forming the lubricant compositions of this invention, it is usually desirable to introduce the additive ingredients into the base oil with stirring and application of mildly elevated temperatures, as this facilitates the dissolution of the components in the oil and achievement of product uniformity.

10

**THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:**

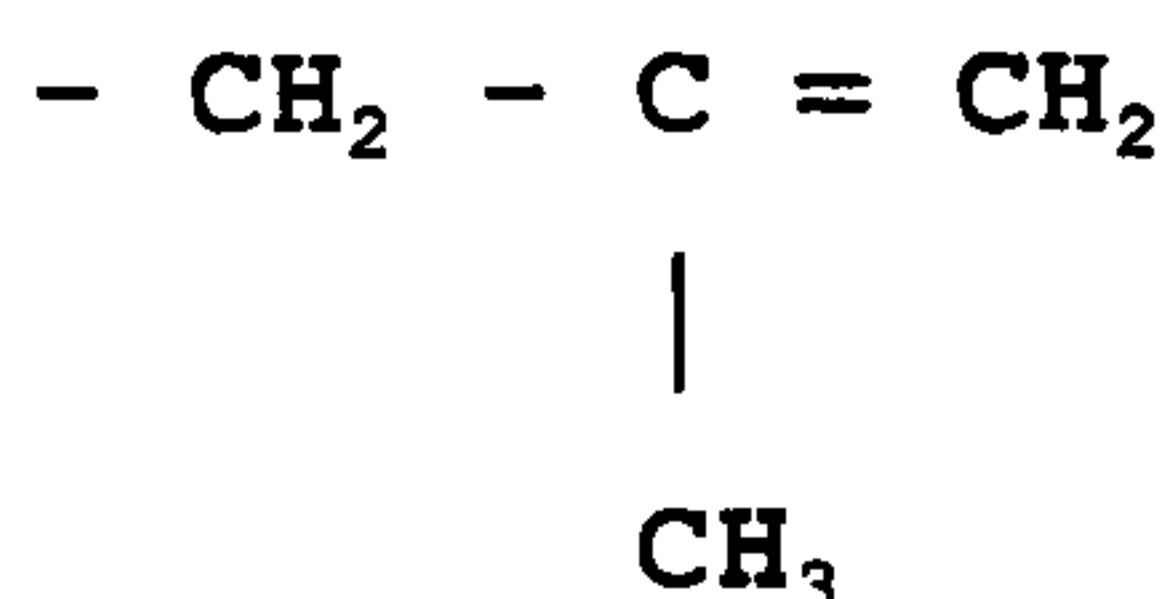
1. A process for preparing a succinic derivative composition which comprises

(A) preparing a substituted succinic acylating agent by a process which comprises reacting (i) an aliphatic polymer of a lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula



wherein R and R' are independently -OH, -O-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process being further defined in that:

(a) the aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the polyisobutene content of such polymer having an end group represented by the formula



(b) the mole ratio of said acidic reactant(s) : said polymer(s) is at least 1 : 1;

(c) the reaction mixture is maintained under a pressure which is greater than 1 atmosphere during a portion of the reaction period; and

(d) said acylating agent is characterized by having an average total tar rating that is at least 25% lower than the average total tar rating of a corresponding product made in the same way under the same reaction

conditions using a polyisobutene containing up to 10% of the above-depicted end group; and

(B) reacting said acylating agent with a combination of an amine having a primary or secondary amino group and an alcohol, the components of said combination being reacted with said acylating agent concurrently or sequentially in any order.

2. A process in accordance with claim 1 wherein the components of said combination are a polyamine having a primary amino group and polyhydric alcohol.

3. A process in accordance with Claim 1 wherein the components of said combination comprise tetraethylene pentamine and pentaerythritol or tris(hydroxymethyl)aminomethane and pentaerythritol.

4. A process in accordance with Claim 1, 2 or 3 wherein at least 75% of said aliphatic polymer is polyisobutene having said end group.

5. A process in accordance with Claim 1, 2, 3, or 4 wherein the entire reaction of (A) is conducted under a pressure which is greater than 1 atmosphere.

6. A process in accordance with Claim 1, 2, 3, 4 or 5 conducted such that the pressure on the reaction mixture in (A) decreases after passing through an initial peak pressure, and then increases to another elevated pressure that is higher than the initial peak pressure.

7. A process for preparing a succinic derivative composition which comprises

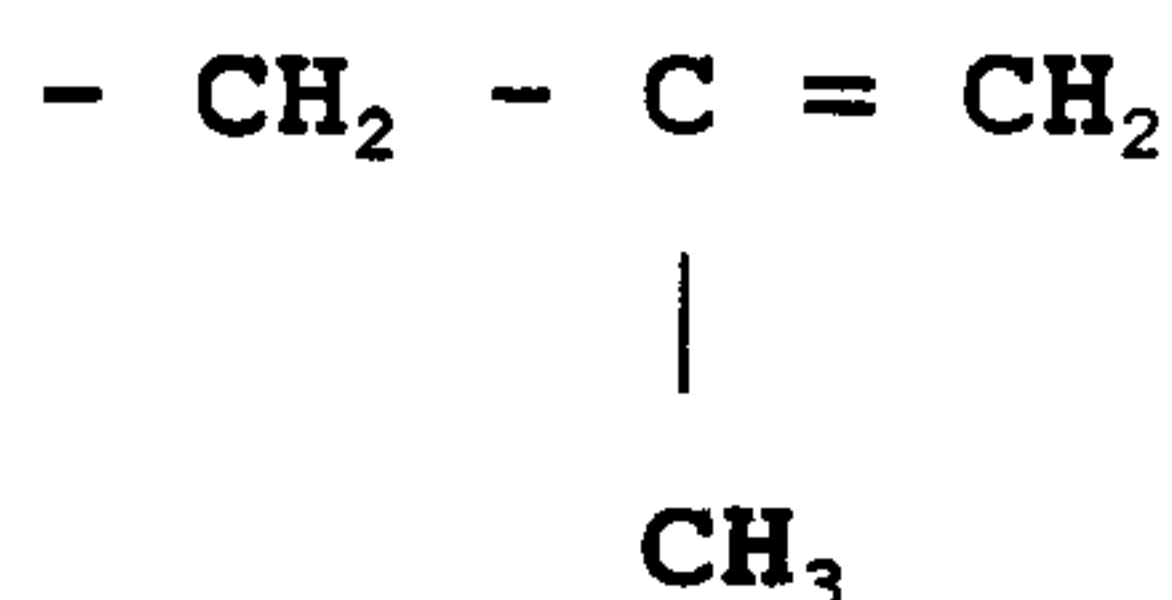
(A) preparing a substituted succinic acylating agent by a process which comprises reacting (i) an aliphatic polymer of a

lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula



wherein R and R' are independently -OH, -O-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process being further defined in that:

- (a) the aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the polyisobutene content of such polymer having an end group represented by the formula



- (b) the mole ratio of said acidic reactant(s) : said polymer(s) is at least 1 : 1;
- (c) the reaction mixture is maintained at a temperature in the range of 200° to 265°C and under a pressure in the range of 4 to 50 psig during a portion of the reaction period; and
- (d) said acylating agent is characterized by having an average total tar rating that is at least 25% lower than the average total tar rating of a corresponding product made in the same way under the same reaction conditions using a polyisobutene containing up to 10% of the above-depicted end group; and

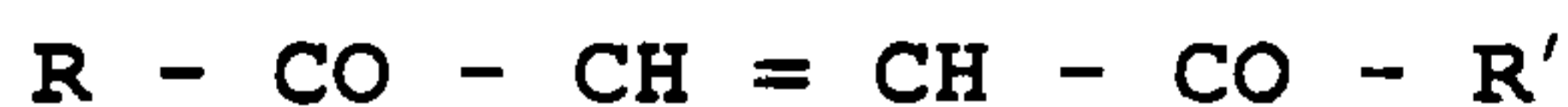
(B) reacting said acylating agent with a combination of an amine having a primary or secondary amino group and an alcohol at a temperature within the range of 100° to 250°C, the components of said combination being reacted with said acylating agent concurrently or sequentially in any order.

8. A process in accordance with any one of Claims 1-7 wherein the mole ratio of said acidic reactant(s) : said polymer(s) is such that the product contains a chemically combined form an average of less than 1.3 moles of said acid groups per mole of polymer chains chemically combined therewith.

9. The use of a succinic derivative composition of any one of Claims 1-8 as a dispersant additive in formulating a lubricant composition.

10. A composition which comprises

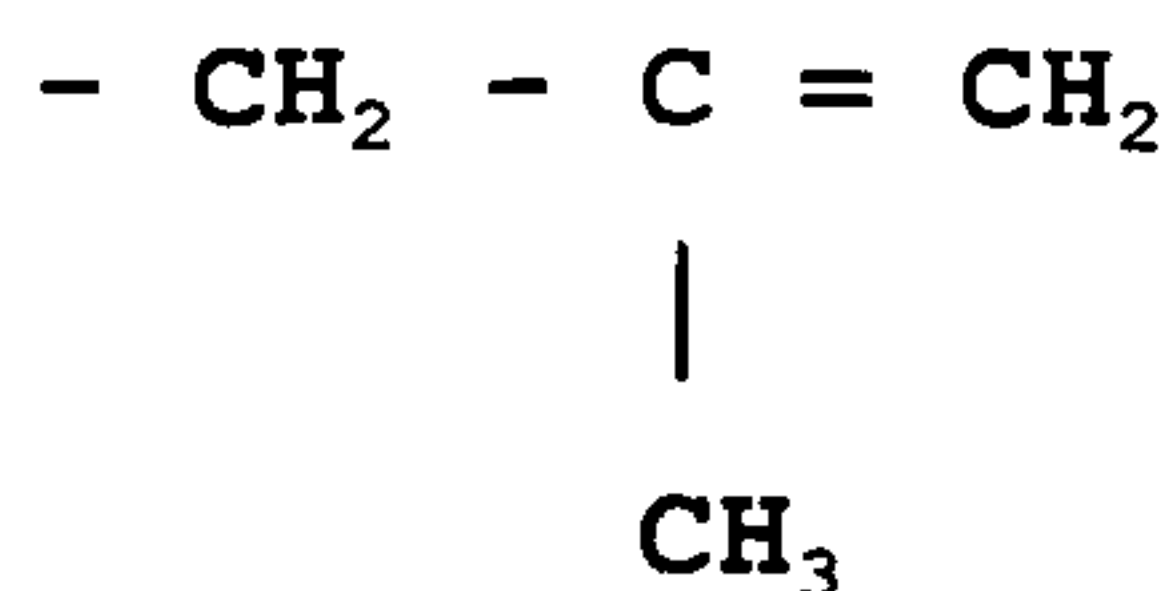
- A) oil of lubricating viscosity;
- B) a carboxylic derivative composition produced by reacting a substituted succinic acylating agent with a reactant selected from the group consisting of (1) an amine having a primary amino group, (2) an alcohol, and (3) a combination of an amine having a primary amino group and an alcohol, the components of (3) being reacted with said substituted succinic acylating agent concurrently or sequentially in any order, said succinic acylating agent being prepared by reacting (i) an aliphatic polymer of a lower olefin, and (ii) an acidic reactant or a mixture of two or more acidic reactants represented by the general formula



wherein R and R' are independently -OH, -O-lower alkyl, a halogen atom, or taken together are a single oxygen atom; the process of preparing said succinic acylating agent being further defined in that:

- a) the aliphatic polymer is comprised predominantly or entirely of polyisobutene, at least 50% of the

polyisobutene content of such polymer having an end group represented by the formula



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b) the mole ratio of said acidic reactant(s) : said polymer(s) is at least 1 : 1; and

c) the reaction mixture is maintained under a pressure which is greater than 1 atmosphere during a portion of the reaction period; and

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C) i) one or more oil-soluble zinc hydrocarbyl dithiophosphates;

ii) one or more oil-soluble or oil-dispersible alkali or alkaline-earth metal-containing detergents;

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iii) one or more oil-soluble or oil-dispersible sulfur-containing antiwear agents, extreme pressure agents, or both antiwear agents and extreme pressure agents; or

iv) an oil-soluble metal-free phosphorus-containing antiwear agent or an extreme pressure agent, or mixtures of two or more of i), ii), iii), and iv).

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11. A composition according to Claim 10 wherein the antiwear agent or the extreme pressure agent of component C(iv) is an oil-soluble metal-free phosphorous and nitrogen containing antiwear agent or extreme pressure agent.

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12. A composition according to Claim 10 or 11 wherein component C(iv) is an amine salt of a dihydrocarbyl ester of a thiophosphoric acid.

