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(54) Title: IMPROVED PROCESS FOR MAKING POLYALKYLENE/MALEIC ANHYDRIDE COPOLYMER

(57) Abstract: A process is provided for preparing a mixture of (1) a copolymer of a polyalkene and an unsaturated acidic reagent and (2) a polyalkenyl derivative of an unsaturated acidic reagent, said process comprising (a) copolymerizing (1) a polyalkene containing alkylvinylidene isomer and non-alkylvinylidene isomers and (2) an unsaturated acidic reagent under polymerization conditions in the presence of a free radical initiator; and (b) reacting the product of step (a) with an unsaturated acidic reagent at elevated temperature in the presence of a strong acid. The product of the process can be used to make polysuccinimides that are useful in lubricating oil compositions.

1 **IMPROVED PROCESS FOR MAKING POLYALKYLENE/MALEIC ANHYDRIDE**
2 **COPOLYMER**

3 The present invention relates to an improved process for making a copolymer of a
4 polybutene with an unsaturated acidic reagent.

5 **BACKGROUND OF THE INVENTION**

6 Copolymers prepared from polyisobutene and maleic anhydride are known. These
7 copolymers are sometimes referred to as "polyPIBSA". They can be prepared by
8 copolymerizing a polybutene containing a high concentration of the
9 methylvinylidene isomer (along with other polybutene isomers) with an unsaturated
10 acidic reagent such as maleic anhydride using a free radical initiator. Apparently,
11 only the methylvinylidene isomer reacts. If the polybutene contains, e.g., 70 mole
12 percent methylvinylidene isomer, then only 70% conversion to copolymer can be
13 achieved. This results in a less than optimum use of the polybutene starting
14 material.

15 In order to improve the conversion of the polybutene starting material and improve
16 raw material utilization, it has been found that if the polyPIBSA reaction mixture is
17 further reacted with the unsaturated acidic reagent in the presence of a strong acid
18 catalyst, such as a sulfonic acid catalyst, the unreacted polybutene can be
19 converted to polyisobutenyl succinic anhydride. Up to 90-95% conversion of the
20 starting polybutene can be achieved in this way. The resulting product is a mixture
21 of polyPIBSA and acid-catalyzed thermal PIBSA.

22 The resulting mixture of polyPIBSA and acid-catalyzed thermal PIBSA can then be
23 reacted with amines to form succinimides which can be post-treated with ethylene
24 carbonate, boric acid and the like. These products are excellent ashless
25 dispersants for lubricants with outstanding deposit inhibiting properties, and
26 excellent soot thickening properties, and are also useful as fuel additives and as
27 emulsifiers in explosive emulsions.

1 Water-in-oil explosive emulsions typically comprise a continuous organic phase
2 (e.g., a carbonaceous fuel) and a discontinuous aqueous phase containing an
3 oxygen supplying component (e.g., ammonium nitrate). Examples of such water-
4 in-oil explosive emulsions are disclosed in U. S. Patents Nos. 3,447,978;
5 3,765,964; 3,985,593; 4,008,110; 4,097,316; 4,104,092; 4,218,272; 4,259,977;
6 4,357,184; 4,371,408; 4,391,659; 4,404,050; 4,409,044; 4,448,619; 4,453,989; and
7 4,534,809, each of which is incorporated by reference herein.

8 U. S. Patent No. 5,920,031, issued July 6, 1999 to Jahnke, discloses water-in-oil
9 emulsions that are useful as explosives. The emulsions comprise a discontinuous
10 aqueous phase comprising at least one oxygen-supplying component, a continuous
11 organic phase comprising at least one carbonaceous fuel, and a minor emulsifying
12 amount of at least one emulsifier. The emulsifier is the product made by the
13 reaction of component (A) with component (B), component (A) being at least one
14 substituted succinic acylating agent, said substituted succinic acylating agent
15 consisting of substituent groups and succinic groups wherein the substituent
16 groups are derived from a polyalkene, said acylating agents being characterized by
17 the presence within their structure of an average of at least 1.3 succinic groups for
18 each equivalent weight of substituent groups, and component (B) being ammonia
19 and/or at least one mono-amine.

20 SUMMARY OF THE INVENTION

21 The present invention provides a process for preparing a mixture of (1) a
22 copolymer of a polyalkene and an unsaturated acidic reagent and (2) a polyalkenyl
23 derivative of an unsaturated acidic reagent, said process comprising:

- 24 (a) copolymerizing (1) a polyalkene containing alkylvinylidene isomer and
25 non-alkylvinylidene isomers and (2) an unsaturated acidic reagent
26 under polymerization conditions in the presence of a free radical
27 initiator; and
- 28 (b) reacting the product of step (a) with an unsaturated acidic reagent at
29 elevated temperature in the presence of a strong acid.

30 Preferably, the polyalkene is a polybutene. More preferably, the polybutene is a
31 polyisobutene, most preferably wherein at least 50% of said polyisobutene has

methylvinyldiene end groups. Preferably, the polyalkene has a Mn of from 500 to 2500.

Preferably, the unsaturated acidic reagent is maleic anhydride.

5 Preferably, the mole ratio of unsaturated acidic reagent to polyalkene is at least 1.0:1.

Preferably, the strong acid is an oil-soluble, strong organic acid, having a pK_a of less than about 4. More preferably, it is a sulfonic acid, such as an alkyl benzene sulfonic acid, wherein the alkyl group has from 4 to 30 carbon atoms. Preferably, the sulfonic acid is present in an amount in the range of from 0.0025% to 1.0% based on the total weight of polyalkene.

10

The present invention further provides the product produced by a process comprising:

- 15
- (a) copolymerizing (1) a polyalkene containing alkylvinyldiene isomer and non-alkylvinyldiene isomers and (2) an unsaturated acidic reagent under polymerization conditions in the presence of a free radical initiator; and
 - (b) reacting the product of step (a) with an unsaturated acidic reagent at elevated temperature in the presence of a strong acid.

20 Also provided by the present invention is a composition comprising a mixture of (1) a copolymer of a polyalkene and an unsaturated acidic reagent and (2) a polyalkenyl derivative of an unsaturated acidic reagent wherein the weight ratio of copolymer to polyalkenyl derivative is about 0.1-10, and wherein the copolymer and the polyalkenyl derivative are prepared using the process of this invention. This mixture is referred to herein as a "polyPIBSA/acid-catalyzed thermal PIBSA mixture".

25 Further provided by the present invention is a polysuccinimide prepared by reacting a polyPIBSA/acid-catalyzed thermal PIBSA mixture of the present invention with an amine, a polyamine having at least two basic nitrogens, or mixture thereof. The present invention also provides a concentrate comprising 10 to 90 weight percent of such a polysuccinimide and from 90 to 10 weight percent of an organic diluent.

In addition, the present invention provides a lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor amount of such a polysuccinimide. Also provided by the present invention is a post-treated composition prepared by treating such a polysuccinimide under reactive
5 conditions with a cyclic carbonate. Further provided by the present invention is a post-treated composition prepared by treating such a polysuccinimide under reactive conditions with a boron compound.

The present invention further provides a lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor amount of the post-
10 treated composition. Also provided by the present invention is a concentrate comprising 20 to 60 weight percent of the post-treated composition and from 80 to 40 weight percent of an organic diluent.

Also provided by the present invention is a fuel composition comprising a hydrocarbon boiling in the gasoline or diesel range and from about 10 to about
15 10,000 parts per million of post-treated composition of this invention. Further provided is a fuel concentrate comprising an inert, stable oleophilic solvent boiling in the range of 150-400°F and at least 5 percent by weight of the post-treated composition of this invention.

Also provided by the present invention is a polyester prepared by reacting a
20 polyPIBSA/acid-catalyzed thermal PIBSA mixture of the present invention with a polyol.

Also provided by the present invention is a concentrate comprising 10 to 90 weight percent of a polyester and from 90 to 10 weight percent of an organic diluent.

25 Also provided by the present invention is a lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor amount of a polyester.

Also provided by the present invention is a post-treated composition prepared by treating a polyester under reactive conditions with a boron compound.

Also provided by the present invention is a water-in-oil emulsion comprising a discontinuous aqueous phase comprising at least one oxygen-supplying
5 component, a continuous organic phase comprising at least one carbonaceous fuel, and a minor emulsifying amount of at least one emulsifier comprising the product produced by a process comprising (a) copolymerizing (1) a polyalkene containing alkylvinylidene isomer and non-alkylvinylidene isomers and (2) an
10 unsaturated acidic reagent under polymerization conditions in the presence of a free radical initiator, (b) reacting the product of step (a) with an unsaturated acidic reagent at elevated temperature in the presence of a strong acid, and (c) reacting the product of step (b) with ammonia or at least one amine.

DETAILED DESCRIPTION OF THE INVENTION

The process comprises the steps of copolymerizing a polyalkene and an unsaturated acidic reagent, followed by reacting any unreacted polyalkene with the unsaturated acidic reagent at elevated temperature in the presence of a strong acid. The polyalkene comprises a mixture of alkylvinylidene and non-alkylvinylidene isomers. It is believed that the alkylvinylidene isomers participate primarily in the copolymerization reaction, and that any alkylvinylidene isomers remaining after the copolymerization reaction plus the non-alkylvinylidene isomers participate primarily in the second reaction.

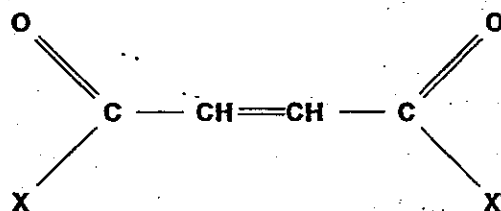
THE POLYALKENE

The polyalkene can be a polymer of a single type of olefin or it can be a copolymer of two or more types of olefins. It contains both alkylvinylidene isomer and non-alkylvinylidene isomers. Preferably, the polyalkene is a polybutene, more preferably a polyisobutene, and most preferably a polyisobutene wherein at least 50%, but less than 100%, of the polyisobutene has methylvinylidene end groups. Preferably, the polyalkene has a number average molecular weight (M_n) of from about 500 to about 2500.

The polyalkene can also be used in combination with a 1-olefin (also known as an "alpha-olefin"). The 1-olefin typically has five or more carbon atoms, preferably about 10 to about 30 carbon atoms. U. S. Patent No. 5,792,729, issued August 11, 1998 to Harrison and Ruhe, discloses the preparation of terpolymers made from a polyalkene, a 1-olefin, and an unsaturated acidic reagent and is incorporated herein by reference in its entirety.

THE UNSATURATED ACIDIC REAGENT

The term "unsaturated acidic reagent" refers to maleic or fumaric reactants of the general formula:



2 wherein X and X' are the same or different, provided that at least one of X and X' is
 3 a group that is capable of reacting to esterify alcohols, form amides, or amine salts
 4 with ammonia or amines, form metal salts with reactive metals or basically reacting
 5 metal compounds and otherwise function as acylating agents. Typically, X and/or X'
 6 is —OH, —O—hydrocarbyl, —OM⁺ where M⁺ represents one equivalent of a metal,
 7 ammonium or amine cation, —NH₂, —Cl, —Br, and taken together X and X' can be
 8 —O— so as to form an anhydride. Preferably, X and X' are such that both
 9 carboxylic functions can enter into acylation reactions. Maleic anhydride is a
 10 preferred unsaturated acidic reactant. Other suitable unsaturated acidic reactants
 11 include electron-deficient olefins such as monophenyl maleic anhydride;
 12 monomethyl, dimethyl, monochloro, monobromo, monofluoro, dichloro and difluoro
 13 maleic anhydride, N-phenyl maleimide and other substituted maleimides;
 14 isomaleimides; fumaric acid, maleic acid, alkyl hydrogen maleates and fumarates,
 15 dialkyl fumarates and maleates, fumaronilic acids and maleanic acids; and
 16 maleonitrile, and fumaronitrile.

17 THE STRONG ACID

18 The term "strong acid" refers to an acid having a pK_a of less than about 4,
 19 preferably -10 to less than +4, more preferably -3 to +2. Preferably, the strong
 20 acid is an oil-soluble, strong organic acid. Representative classes of the oil-soluble
 21 strong acids are represented by maleic acid, malonic acid, phosphoric acid,
 22 thiophosphoric acids, phosphonic acid, thiophosphonic acids, sulfonic acids,
 23 sulfuric acid, and alpha-substituted or nitrilocarboxylic acids wherein the oil-
 24 solubilizing group or groups are hydrocarbyl and contain from 10 to 76, preferably
 25 from 24 to 40, more preferably from 28 to 36 carbon atoms, and the aryl group is
 26 preferably phenyl.

1 Preferably, the strong acid is a sulfonic acid. Still more preferably, the sulfonic acid
2 is an alkyl aryl sulfonic acid. Most preferably, the alkyl group of said alkyl aryl
3 sulfonic acid has from 4 to 30 carbon atoms.

4 Preferably, the sulfonic acid is present in an amount in the range of from 0.0025%
5 to 1.0% based on the total weight of polyalkene.

6 COPOLYMERIZATION CONDITIONS

7 U. S. Patent No. 5,112,507, issued May 12, 1992 to Harrison, discloses
8 copolymerization conditions useful in the practice of this invention, and is
9 incorporated by reference herein in its entirety. In general, the copolymerization
10 reaction may be conducted at a temperature of about -30° C. to about 210° C., and
11 preferably from about 40° C. to about 180° C. The degree of polymerization is
12 inversely proportional to temperature. Accordingly, it may be advantageous to
13 employ lower reaction temperatures. For example, if the reaction is conducted at
14 about 138° C., an average degree of polymerization of about 1.3 is obtained.
15 However, if the reaction is conducted at a temperature of about 40° C., an average
16 degree of polymerization of about 10.5 is obtained.

17 The polyPIBSA can have an apparent succinic ratio greater than 1.3, such as those
18 disclosed in U. S. Patent No. 5,565,528, issued October 15, 1996 to Harrison and
19 Ruhe, which is incorporated herein by reference in its entirety.

20 The reaction may be conducted neat, that is, the polyalkene, the unsaturated acidic
21 reactant and the free radical initiator are combined in the proper ratio and then
22 stirred at the reaction temperature. The unsaturated acidic reagent may be added
23 over time, or all at once.

24 Alternatively, the reaction may be conducted in a diluent. For example, the
25 reactants may be combined in a solvent. Suitable solvents include those in which
26 the reactants and the free radical initiator are soluble and include acetone,
27 tetrahydrofuran, chloroform, methylene chloride, dichloroethane, toluene, dioxane,
28 chlorobenzene, xylenes and the like. PIBSA, polyPIBSA or mixtures thereof may

1 also be used as a solvent for the reaction. See U. S. Patent No. 5,175,225, issued
2 December 29, 1992 to Ruhe, which is incorporated herein by reference in its
3 entirety. Depending upon the particular solvent employed, it may or may not enter
4 into the reaction as a chain transfer agent. After the reaction is complete, volatile
5 components may be stripped off.

6 In general, the copolymerization can be initiated by any free radical initiator. Such
7 initiators are well known in the art. However, the choice of the free radical initiator
8 may be influenced by the reaction temperature employed.

9 The preferred free radical initiators are the peroxide-type polymerization initiators
10 and the azo-type polymerization initiators. Radiation can also be used to initiate
11 the reaction, if desired.

12 The peroxide-type initiator can be organic or inorganic, the organic having the
13 general formula $R^3OOR^{3'}$ where R^3 is any organic radical and $R^{3'}$ is selected from
14 the group consisting of hydrogen and any organic radical. Both R^3 and $R^{3'}$ can be
15 organic radicals, preferably hydrocarbon, aryl and acyl radicals, carrying, if desired,
16 substituents such as halogens. Preferred peroxides include di-tert-butyl peroxide,
17 tert-butyl peroxybenzoate and dicumyl peroxide.

18 Examples of other peroxides, which in no way are limiting, include benzoyl
19 peroxide, lauroyl peroxide, other tertiary butyl peroxides, 2,4-dichloro-benzoyl
20 peroxide, tertiary butyl hydroperoxide, cumene hydroperoxide, diacetyl peroxide,
21 acetyl hydroperoxide, diethylperoxycarbonate, tertiary butyl perbenzoate and the
22 like.

23 The azo-type compounds, typified by alpha, alpha'-azobisisobutyronitrile, are also
24 well known free radical promoting materials. The azo compounds can be defined
25 as those having present in the molecule group $-N=N-$ wherein the balances are
26 satisfied by organic radicals, at least one of which is preferably attached to a
27 tertiary carbon. Other suitable azo compounds include, but are not limited to, p-
28 bromobenzenediazonium fluoroborate, p-tolyldiazoaminobenzene, p-
29 bromobenzenediazonium hydroxide, azomethane, and phenyldiazonium halides. A

1 suitable list of azo-type compounds can be found in U. S. Patent No. 2,551,813,
2 issued May 8, 1951 to Pinkney, which is incorporated herein by reference in its
3 entirety.

4 The amount of initiator to employ, exclusive of radiation, of course, depends to a
5 large extent on the particular initiator chosen, the polyalkene used and the reaction
6 conditions. The initiator must, of course, be soluble in the reaction medium. The
7 usual concentrations of initiator are between 0.001:1 and 0.2:1 moles of initiator
8 per mole of acidic reactant, with preferred amounts between 0.005:1 and 0.10:1.

9 The polymerization temperature must be sufficiently high to break down the initiator
10 to produce the desired free-radicals. For example, using benzoyl peroxide as the
11 initiator, the reaction temperature can be between about 75°C and about 90°C,
12 preferably between about 80°C and about 85°C. Higher and lower temperatures
13 can be employed, a suitable broad range of temperatures being between about
14 20°C and about 200°C, with preferred temperatures between about 50°C and about
15 180°C.

16 The reaction pressure should be sufficient to maintain the solvent in the liquid
17 phase. Pressures can therefore vary between about atmospheric and 100 psig or
18 higher, but the preferred pressure is atmospheric.

19 The reaction time is usually sufficient to result in the substantially complete
20 conversion of the acidic reactant and high molecular weight olefin to copolymer.
21 The reaction time is suitable between one and 24 hours, with preferred reaction
22 times between two and ten hours.

23 As noted above, the subject reaction is a solution-type polymerization reaction. The
24 high molecular weight olefin, acidic reactant, solvent and initiator can be brought
25 together in any suitable manner. The important factors are intimate contact of the
26 high molecular weight olefin and acidic reactant in the presence of a free-radical
27 producing material. The reaction, for example, can be conducted in a batch system
28 where the high molecular weight olefin is added all initially to a mixture of acidic
29 reactant, initiator and solvent or the high molecular weight olefin can be added

1 intermittently or continuously to the reaction pot. Alternatively, the reactants may be
2 combined in other orders, for example, acidic reactant and initiator may be added
3 to high molecular weight olefin and solvent in the reaction pot. In another manner,
4 the components in the reaction mixture can be added continuously to a stirred
5 reactor with continuous removal of a portion of the product to a recovery train or to
6 other reactors in series. The reaction can also suitably take place in a coil-type
7 reactor where the components are added at one or more point along the coil.

8 THE PROCESS FOR PREPARING POLYALKENYL DERIVATIVES

9 In the preparation of the polyalkenyl derivative, the mole ratio of unsaturated acidic
10 reagent to polyalkene is preferably at least 1.0:1. More preferably, that mole ratio is
11 from 1.0:1 to 4.0:1.

12 Preferably, the unsaturated acidic reagent is added over a period of time period
13 (such as from ½ to 3 hours) or all at once.

14 The reaction is conducted with an excess of unsaturated acidic reagent at elevated
15 temperatures in the presence of a strong acid to convert at least some of the
16 unreacted polyalkene to additional polyalkenyl derivative of an unsaturated acidic
17 reagent. This reaction is an ene reaction, not polymerization. The product of this
18 reaction is referred to herein as "acid-catalyzed thermal PIBSA".

19 The temperature of the reaction in the second step (the ene reaction) can vary over
20 a wide range. Preferably, the temperature is in the range of from 180° to 240°C.

21 The pressure can be atmospheric, sub-atmospheric, or super-atmospheric.

22 Preferably, the pressure is super-atmospheric.

23 When the reaction is complete, the unreacted unsaturated acidic reagent is
24 removed. Preferably, the reaction medium is cooled as soon as the unreacted
25 unsaturated acidic reagent has been removed. The reaction product may contain
26 some tar or resin which is believed to be polymaleic anhydride by-product. The
27 insoluble portion of this by-product can be removed by filtration, but some may
28 remain in the product as a soluble resin.

1 By using the two step process of this invention, conversion of the polyalkene can
2 be as high as 90-95%. This has the advantage that it minimizes the amount of
3 unreacted polyalkene in the final reaction product. Unreacted polyalkene tends to
4 increase the viscosity of a dispersant at constant nitrogen levels, often requiring the
5 addition of a low viscosity diluent oil. The present invention permits the use of less
6 (or no) diluent oil, as well as providing higher utilization of the polyalkene.

7 PROCESS FOR PREPARING POLYSUCCINIMIDES

8 A polysuccinimide can be prepared by reacting the polyPIBSA/acid-catalyzed
9 thermal PIBSA mixture produced by the present invention with either an amine or a
10 polyamine, under reactive conditions. The amine or polyamine should be
11 employed in amounts such that there are 0.1 to 1.5 equivalents of amine or
12 polyamine per equivalent of acidic groups in the polyPIBSA/acid-catalyzed thermal
13 PIBSA mixture. Preferably, a polyamine is used having at least three nitrogen
14 atoms and 4 to 20 carbon atoms.

15 It may be desirable to conduct the reaction in an inert organic solvent. Optimum
16 solvents will vary and can be determined from literature sources or routine
17 experiments. Typically, the reaction is conducted at temperatures in the range of
18 from about 60°C. to 180°C., preferably 150°C. to 170°C. for from about 1 to 10
19 hours, preferably 2 to 6 hours. Typically, the reaction is conducted at about
20 atmospheric pressure; however, higher or lower pressures can also be used
21 depending on the reaction temperature desired and the boiling point of the
22 reactants or solvent.

23 Water, present in the system or generated by this reaction, is preferably removed
24 from the reaction system during the course of the reaction via azeotroping or
25 distillation. After reaction completion, the system can be stripped at elevated
26 temperatures (typically 100°C to 250°C) and reduced pressures to remove any
27 volatile components that may be present in the product.

28 An amine or, preferably, a polyamine is used. Preferably, the polyamine has at
29 least three amine nitrogen atoms per molecule, and more preferably, 4 to 12 amine

1 nitrogens per molecule. Most preferred are polyamines having from about 6 to 10
2 nitrogen atoms per molecule.

3 Preferred polyalkene polyamines also contain from about 4 to 20 carbon atoms,
4 preferably from 2 to 3 carbon atoms per alkylene unit. The polyamine preferably
5 has a carbon-to-nitrogen ratio of from 1:1 to 10:1.

6 Examples of suitable polyamines that can be used to form the succinimides of this
7 invention include the following: tetraethylene pentamine, pentaethylene hexamine,
8 Dow E-100 heavy polyamine ($M_n=303$, available from Dow Chemical Company),
9 and Union Carbide HPA-X heavy polyamine ($M_n=275$, available from Union Carbide
10 Corporation). Such polyamines encompass isomers, such as branched-chain
11 polyamines, and substituted polyamines, including hydrocarbyl-substituted
12 polyamines. HPA-X heavy polyamine contains an average of approximately 6.5
13 amine nitrogen atoms per molecule.

14 The polyamine reactant may be a single compound, but typically will be a mixture
15 of compounds reflecting commercial polyamines. Typically, the commercial
16 polyamine will be a mixture in which one or several compounds predominate with
17 the average composition indicated. For example, tetraethylene pentamine
18 prepared by the polymerization of aziridine or the reaction of dichloroethylene and
19 ammonia will have both lower and higher amine members, e.g., triethylene
20 tetramine, substituted piperazines and pentaethylene hexamine, but the
21 composition will be largely tetraethylene pentamine and the empirical formula of the
22 total amine composition will closely approximate that of tetraethylene pentamine.

23 Other examples of suitable polyamines include admixtures of amines of various
24 molecular weights. Included are mixtures of diethylene triamine and heavy
25 polyamine. A preferred polyamine admixture is a mixture containing 20% by weight
26 diethylene triamine and 80% by weight heavy polyamine.

27 If an amine, i.e., a monoamine, is employed, it should be a primary amine,
28 secondary amine, or mixture thereof. Preferably, the amine will have at least 10
29 carbon atoms, more preferably between 12 and 18 carbon atoms. Although

1 aromatic amines may be employed, it is preferred to use aliphatic amines. Both
2 saturated and unsaturated amines may be employed. Preferred amines include
3 aliphatic primary amines. Examples of suitable amines include, but are not limited
4 to, octadecylamine and dodecylamine. An example of a suitable mixture of amines
5 is tallowamine (a partially saturated mixture of amines comprised mainly of C₁₈
6 amines).

7 Mixtures of monoamines and polyamines may be used. Also, polyoxyalkylene
8 polyamines (for example, materials supplied under the trade name Jeffamine) and
9 aminoalcohols can also be suitably used.

10 PROCESS FOR PREPARING POLYESTERS

11 Polyesters can be prepared by reacting the polyPIBSA/acid-catalyzed thermal
12 PIBSA mixture produced by the present invention with a polyol, under reactive
13 conditions. The polyols have the formula Rⁿ(OH)_x where Rⁿ is a hydrocarbon
14 radical and x is an integer representing the number of hydroxy radicals and has a
15 value of from 2 to about 10. The polyols preferably contain less than 30 carbon
16 atoms, and have from 2 to about 10, preferably 3 to 6, hydroxy radicals. They are
17 illustrated by, for example, alkylene glycols and poly(oxyalkylene) glycols such as
18 ethylene glycol, di(ethylene glycol), tri(ethylene glycol), di(propylene glycol),
19 tri(butylene glycol), penta(ethylene glycol), and other poly(oxyalkylene) glycols
20 formed by the condensation of two or more moles of ethylene glycol, propylene
21 glycol, octylene glycol, or a like glycol having up to 12 carbon atoms in the alkylene
22 radical. Other useful polyhydric alcohols include glycerol, pentaerythritol, 2,4-
23 hexanediol, pinacol, erythritol, arabitol, sorbitol, mannitol, 1,2-cyclohexanediol,
24 xylylene glycol, and 1,3,5-cyclohexanetriol. Other useful polyols are disclosed in U.
25 S. Patent No. 4,034,038, issued July 5, 1977 to Vogel, which is incorporated by
26 reference in its entirety.

27 Esterification can be effected at a temperature of about 100°C to about 180°C,
28 preferably about 150°C to about 160°C. Ordinarily, the reaction is carried out at
29 substantially atmospheric pressure, although pressures above atmospheric may be
30 employed with more volatile reactants. Usually, stoichiometric amounts of

1 reactants are employed. The reaction may be run in the absence of a catalyst, or
2 in the presence of an acid-type catalyst such as mineral acids, sulfonic acids, Lewis
3 type acids and the like. Suitable reaction conditions and catalysts are disclosed in
4 U. S. Patent No. 3,155,686, issued November 3, 1964 to Prill et al., which is
5 incorporated by reference in its entirety.

6 POST-TREATMENT OF POLYSUCCINIMIDES

7 The dispersancy of the compositions of this invention is generally further improved
8 by reaction with a cyclic carbonate. The resulting post-treated product has one or
9 more nitrogens of the polyamino moiety substituted with a hydroxy hydrocarbyl
10 oxycarbonyl, a hydroxy poly(oxyalkylene) oxycarbonyl, a hydroxyalkylene,
11 hydroxyalkylenepoly(oxyalkylene), or mixture thereof.

12 The cyclic carbonate post-treatment is conducted under conditions sufficient to
13 cause reaction of the cyclic carbonate with secondary amino groups of the
14 polyamino substituents. Typically, the reaction is conducted at temperatures of
15 about 0°C to 250°C, preferably from 100°C to 200°C. Generally, best results are
16 obtained at temperatures of from about 150°C to 180°C.

17 The reaction may be conducted neat, and may or may not be conducted in the
18 presence of a catalyst (such as an acidic, basic or Lewis acid catalyst). Depending
19 on the viscosity of the reactants, it may be desirable to conduct the reaction using
20 an inert organic solvent or diluent, e.g., toluene or xylene. Examples of suitable
21 catalysts include phosphoric acid, boron trifluoride, alkyl or aryl sulfonic acid, and
22 alkali or alkaline earth carbonate.

23 A particularly preferred cyclic carbonate is 1,3-dioxolan-2-one (ethylene carbonate)
24 because it affords excellent results and also because it is readily available
25 commercially.

26 The molar charge of cyclic carbonate employed in the post-treatment reaction is
27 preferably based upon the theoretical number of basic nitrogen atoms contained in
28 the polyamino substituent of the succinimide. Thus, when one equivalent of

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1 tetraethylene pentamine is reacted with two equivalents of succinic anhydride, the
2 resulting bis-succinimide will theoretically contain three basic nitrogen atoms.
3 Accordingly, a molar charge ratio of 2 would require that two moles of cyclic
4 carbonate be added for each basic nitrogen, or in this case 6 moles of cyclic
5 carbonate for each mole equivalent of succinimide. Mole ratios of the cyclic
6 carbonate to the basic amine nitrogen are typically in the range of from about 1:1 to
7 about 4:1; preferably from about 2:1 to about 3:1.

8 The polysuccinimide composition of this invention, including the post-treated
9 compositions described above, can also be reacted with boric acid or a similar
10 boron compound to form borated dispersants having utility within the scope of this
11 invention. In addition to boric acid, examples of suitable boron compounds include
12 boron oxides, boron halides and esters of boric acid. Generally, from about 0.1
13 equivalent to about 1 equivalent of boron compound per equivalent of basic
14 nitrogen or hydroxyl in the compositions of this invention may be employed.

15 LUBRICATING OIL COMPOSITIONS AND CONCENTRATES

16 The compositions of this invention are useful as detergent and dispersant additives
17 in lubricating oils. In general, when employed in crankcase oils they are usually
18 present from about 1 to about 10 percent by weight (on an actives basis) of the
19 total composition, and preferably less than about 5 percent by weight (on an
20 actives basis). Actives basis indicates that only the active ingredients of this
21 invention are considered when determining the amount of the additive relative to
22 the remainder of a composition. Diluents and any other inactives, such as
23 unreacted polyalkene, are excluded. Unless otherwise indicated, in describing the
24 lubricating oil and final compositions or concentrates, active ingredient contents are
25 intended with respect to the polysuccinimides.

26 The lubricating oil used with the additive compositions of this invention may be
27 mineral or synthetic oils of lubricating viscosity and preferably suitable for use in the
28 crankcase of an internal combustion engine. Crankcase lubricating oils typically
29 have a viscosity of about 1300 cSt at 0°F. (-17.8°C) to 22.7 cSt at 210°F. (99°C).
30 Mineral oil for use as the base oil in this invention includes paraffinic, naphthenic

1 and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils
2 include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic
3 hydrocarbon oils include polymers of alpha olefins having the proper viscosity.
4 Especially useful are the hydrogenated liquid oligomers of C₆ to C₁₂ alpha olefins,
5 such as 1-decene trimer. Likewise, alkyl benzenes of proper viscosity such as
6 didodecyl benzene can be used. Useful synthetic esters include the esters of both
7 monocarboxylic acids and polycarboxylic acids as well as monohydroxy alkanols
8 and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaprate,
9 di-2-ethylhexyl adipate, dilaurylsebacate and the like. Complex esters prepared
10 from mixtures of mono and dicarboxylic acid and mono and dihydroxy alkanols can
11 also be used.

12 Blends of hydrocarbon oils and synthetic oils are also useful. For example, blends
13 of 10 to 25 weight percent hydrogenated 1-decene trimer with 75 to 90 weight
14 percent 150 SUS (100°F.) mineral oil gives an excellent lubricating oil base.

15 Other additives which may be present in the formulation include detergents
16 (overbased and non-overbased), rust inhibitors, foam inhibitors, metal deactivators,
17 pour point depressants, antioxidants, wear inhibitors, zinc dithiophosphates and a
18 variety of other well known additives.

19 It is also contemplated that the polysuccinimides of this invention may be employed
20 as dispersants and detergents in hydraulic fluids, marine crankcase lubricants and
21 the like. In general, when so employed, the polysuccinimide is added at from 0.1 to
22 5 percent by weight (on an active polysuccinimide basis) to the oil, and preferably
23 at from 0.5 to 5 weight percent (on an active polysuccinimide basis).

24 Additive concentrates are also included within the scope of this invention. The
25 concentrates of this invention usually include from 90 to 10 percent, preferably 20
26 to 60 weight percent, of an organic liquid diluent and from 10 to 90 weight percent,
27 preferably 80 to 40 weight percent, (on a dry basis) of the additive of this invention.
28 Typically, the concentrates contain sufficient diluent to make them easy to handle
29 during shipping and storage. Suitable diluents for the concentrates include any
30 inert diluent, preferably an oil of lubricating viscosity, so that the concentrate may

1 be readily mixed with lubricating oils to prepare lubricating oil compositions.
2 Suitable lubricating oils which can be used as diluents typically have viscosities in
3 the range from about 1300 cSt at 0°F. (-17.8°C) to 22.7 cSt at 210°F. (99°C),
4 although an oil of lubricating viscosity can be used.

5 FUEL COMPOSITIONS AND CONCENTRATES

6 When used in fuels, the proper concentration of the additive that is necessary to
7 achieve the desired detergency is dependent upon a variety of factors including the
8 type of fuel used, the presence of other detergents or dispersants or other
9 additives, etc. Generally, however, the range of concentration of the additive in the
10 base fuel is 10 to 10,000 weight parts per million, preferably from 30 to 5,000 parts
11 per million of the additive. If other detergents are present, a lesser amount of the
12 additive may be used. The additives described herein may be formulated as a fuel
13 concentrate, using an inert stable oleophilic solvent boiling in the range of about
14 150-400°F (65.6-204.4°C). Preferred solvents boil in the gasoline or diesel fuel
15 range. Preferably, an aliphatic or an aromatic hydrocarbon solvent is used, such
16 as a benzene, toluene, xylene or higher-boiling aromatics or aromatic thinners.
17 Aliphatic alcohols of about 3 to 8 carbon atoms, such as isopropanol,
18 isobutylcarbinol, n-butanol and the like in combination with hydrocarbon solvents
19 are also suitable for use with the fuel additive. In the fuel concentrate, the amount
20 of the additive will be ordinarily at least 5 percent by weight and generally not
21 exceed 70 percent by weight, preferably from 5 to 50 and more preferably from 10
22 to 25 weight percent.

23 EXPLOSIVE EMULSIONS

24 In one embodiment, the invention is directed to water-in-oil emulsions that are
25 useful as explosives. These emulsions comprise a discontinuous aqueous phase
26 comprising at least one oxygen-supplying component, a continuous organic phase
27 comprising at least one carbonaceous fuel, and a minor emulsifying amount of at
28 least one emulsifier. The emulsifier comprises the product produced by a process
29 comprising (a) copolymerizing (1) a polyalkene containing alkylvinylidene isomer
30 and non-alkylvinylidene isomers and (2) an unsaturated acidic reagent under

1 polymerization conditions in the presence of a free radical initiator, (b) reacting the
2 product of step (a) with an unsaturated acidic reagent at elevated temperature in
3 the presence of a strong acid, and (c) reacting the product of step (b) with ammonia
4 or at least one amine.

5 The term "emulsion" as used herein refers to not only water-in-oil emulsions, but
6 also compositions derived from such emulsions wherein, at temperatures below
7 that at which the emulsion is formed, the discontinuous phase is solid or in the form
8 of droplets of super-cooled liquid. This term also covers compositions derived from
9 or formulated as such water-in-oil emulsions that are in the form of gelatinous or
10 semi-gelatinous compositions.

11 The continuous organic phase is preferably present at a level of at least 2% by
12 weight, more preferably in the range of about 2% to about 15% by weight, more
13 preferably in the range of about 3.5% to about 10% by weight, more preferably
14 about 5% to about 8% by weight based on the total weight of the water-in-oil
15 emulsion. The discontinuous aqueous phase is preferably present at a level of at
16 least about 85% by weight, more preferably at a level in the range of about 85% to
17 about 98% by weight, more preferably about 92% to about 95% by weight based
18 on the total weight of the emulsion. The emulsifier is preferably present at a level
19 in the range of about 5% to about 95% by weight, more preferably about 5% to
20 about 50% by weight, more preferably about 5% to about 20% by weight, more
21 preferably about 10% to about 20% by weight based on the weight of the organic
22 phase. The oxygen-supplying component is preferably present at a level in the
23 range of about 70% to about 95% by weight, , more preferably about 75% to about
24 92% by weight, more preferably about 78% to about 90% by weight based on the
25 total weight of the aqueous phase. The water is preferably present at a level in the
26 range of about 5% to about 30% by weight, more preferably about 8% to about
27 25% by weight, more preferably about 10% to about 22% by weight based on the
28 weight of the aqueous phase.

29 The carbonaceous fuel that is useful in the emulsions of this invention can include
30 most hydrocarbons, foe example, paraffinic, olefinic, naphthenic, aromatic,

1 saturated or unsaturated hydrocarbons, and is typically in the form of an oil or wax
2 or a mixture thereof. In general, the carbonaceous fuel is a water-immiscible,
3 emulsifiable hydrocarbon that is either liquid or liquefiable at a temperature of up to
4 about 95° C, and preferably between about 40° C and about 75° C. Oils from a
5 variety of sources, including natural and synthetic oils and mixtures thereof can be
6 used as the carbonaceous fuel.

7 Natural oils include animal oils and vegetable oils, as well as solvent-refined or
8 acid-refined mineral oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic
9 types. Oils derived from coal or shale are also useful. Synthetic oils include
10 hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and
11 interpolymerized olefins, alkyl benzenes, polyphenyls and the like.

12 Another suitable class of synthetic oils that can be used comprises the esters of
13 dicarboxylic acids (e.g., phthalic acid, sebacic acid, alkyl succinic acid, maleic acid,
14 azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid
15 dimer, malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl
16 alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol
17 monoether, propylene glycol, pentaerythritol, etc.). Specific examples of these
18 esters include, but are not limited to, dibutyl adipate, di(2-ethylhexyl) sebacate, di-
19 n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, di-n-hexyl fumarate and the
20 like.

21 Silico-based oils such as polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxy-siloxane
22 oils and silicate oils comprise another class of useful oils. Diesel fuel can also be
23 used as the oil.

24 The carbonaceous fuel can be any wax having a melting point of at least about 25°
25 C, such as petrolatum wax, microcrystalline wax, paraffin wax, mineral waxes such
26 as ozocerite and monntan wax, animal waxes such as spermacetic wax, and insect
27 waxes such as beeswax and Chinese wax. Preferred waxes are blends of
28 microcrystalline wax and paraffin wax.

1 In one embodiment, the carbonaceous fuel includes a combination of a wax and an
2 oil. The wax content can be at least about 25% and preferably in the range of
3 about 25% to about 90% by weight of the organic phase, and the oil content can be
4 at least about 10% and preferably ranges from about 10% to about 75% by weight
5 of the organic phase.

6 Other examples of carbonaceous fuels useful in this invention are disclosed in
7 aforementioned U. S. Patent No. 5,920,031, which is incorporated by reference
8 herein in its entirety.

9 The oxygen-supplying component is preferably at least one inorganic oxidizer salt
10 such as ammonium, alkali or alkaline earth metal nitrate, chlorate or perchlorate.
11 Examples include ammonium nitrate, sodium nitrate, calcium nitrate, ammonium
12 chlorate, sodium perchlorate and ammonium perchlorate. Ammonium nitrate is
13 preferred. Mixtures of ammonium nitrate and sodium or calcium nitrate are also
14 useful. In one embodiment, the inorganic oxidizer salt principally ammonium
15 nitrate, although up to about 25% by weight of the oxidizer phase can comprise
16 either another inorganic nitrate (e.g., alkali or alkaline earth metal nitrate) or an
17 inorganic perchlorate (e.g., ammonium perchlorate or an alkali or alkaline earth
18 metal perchlorate) or a mixture thereof.

19 The emulsifiers useful in the water-in-oil emulsions of this invention comprise the
20 product produced by a process comprising (a) copolymerizing (1) a polyalkene
21 containing alkylvinylidene isomer and non-alkylvinylidene isomers and (2) an
22 unsaturated acidic reagent under polymerization conditions in the presence of a
23 free radical initiator, (b) reacting the product of step (a) with an unsaturated acidic
24 reagent at elevated temperature in the presence of a strong acid, and (c) reacting
25 the product of step (b) with ammonia or at least one amine.

26 The amines useful in making the emulsifiers include primary amines, secondary
27 amines and tertiary mono-amines, with the secondary and tertiary amines being
28 preferred and the tertiary amines being particularly useful. Hydroxy mono-amines,
29 especially tertiary alkanol monoamines, are useful. Mixtures of two or more amines
30 can be used.

1
2 The amines can be aliphatic, cycloaliphatic, aromatic or heterocyclic, including
3 aliphatic-substituted aromatic, aliphatic-substituted cycloaliphatic, aliphatic-
4 substituted heterocyclic, cycloaliphatic-substituted aliphatic, cycloaliphatic-
5 substituted aromatic, cycloaliphatic-substituted heterocyclic, aromatic-substituted
6 aliphatic, aromatic-substituted cycloaliphatic, aromatic-substituted heterocyclic,
7 heterocyclic-substituted aliphatic, heterocyclic-substituted cycloaliphatic and
8 heterocyclic-substituted aromatic amines. These amines may be saturated or
9 unsaturated. If unsaturated, the amine is preferably free from acetylenic
10 unsaturation. The amines may also contain non-hydrocarbon substituents or
11 groups as long as these groups do not significantly interfere with the reaction of the
12 amines. Such non-hydrocarbon substituents or groups include lower alkoxy, lower
13 alkyl, mercapto, nitro, and interrupting groups such as -O- and -S- (e.g., as in such
14 groups as $-\text{CH}_2 \text{CH}_2 -\text{X}-\text{CH}_2 \text{CH}_2-$ where X is -O- or -S-).

15
16 With the exception of the high molecular weight hydrocarbyl-substituted amines
17 described more fully hereinafter, the amines used in this invention ordinarily contain
18 less than about 40 carbon atoms in total and usually not more than about 20
19 carbon atoms in total.

20
21 Aliphatic monoamines include mono-aliphatic, di-aliphatic and tri-aliphatic
22 substituted amines wherein the aliphatic groups can be saturated or unsaturated
23 and straight or branched chain. Such amines include, for example, mono-, di- and
24 tri-alkyl-substituted amines; mono-, di- and tri-alkenyl-substituted amines; amines
25 having one or more N-alkenyl substituents and one or more N-alkyl substituents,
26 and the like. The total number of carbon atoms in these aliphatic monoamines
27 preferably does not exceed about 40 and usually does not exceed about 20 carbon
28 atoms. Specific examples of such monoamines include ethylamine, di-ethylamine,
29 tri-ethylamine, n-butylamine, di-n-butylamine, alkylamine, isobutylamine,
30 cocoamine, stearylamine, laurylamine, methyl-laurylamine, oleylamine, N-methyl-
31 octylamine, dodecylamine, octadecylamine, and the like. Examples of
32 cycloaliphatic-substituted aliphatic amines, aromatic-substituted aliphatic amines,
33 and heterocyclic-substituted aliphatic amines, include 2-(cyclohexyl)-ethylamine,

1 benzylamine, phenylethylamine, and 3-(furylpropyl) amine.

2

3 Cycloaliphatic monoamines are those monoamines wherein there is one
4 cycloaliphatic substituent attached directly to the amino nitrogen through a carbon
5 atom in the cyclic ring structure. Examples of cycloaliphatic monoamines include
6 cyclohexylamines, cyclopentylamines, cyclohexenylamines, cyclopentenylamines,
7 N-ethyl-cyclohexylamines, dicyclohexylamines, and the like. Examples of aliphatic-
8 substituted, aromatic-substituted, and heterocyclic-substituted cycloaliphatic
9 monoamines include propyl-substituted cyclohexylamines, phenyl-substituted
10 cyclopentylamines and pyranyl-substituted cyclohexylamine.

11

12 Suitable aromatic amines include those monoamines wherein a carbon atom of the
13 aromatic ring structure is attached directly to the amino nitrogen. The aromatic ring
14 will usually be a mononuclear aromatic ring (i.e., one derived from benzene) but
15 can include fused aromatic rings, especially those derived from naphthylene.
16 Examples of aromatic monoamines include aniline, di(para-methylphenyl) amine,
17 naphthylamine, N-(n-butyl) aniline, and the like. Examples of aliphatic-substituted,
18 cycloaliphatic-substituted, and heterocyclic-substituted aromatic monoamines
19 include para-ethoxyaniline, para-dodecylaniline, cyclohexyl-substituted
20 naphthylamine and thienyl-substituted aniline.

21

22 Heterocyclic mono-amines can also be used. As used herein, the terminology
23 "heterocyclic mono-amine(s)" is intended to describe those heterocyclic amines
24 containing at least one primary, secondary or tertiary amino group and at least one
25 nitrogen as a heteroatom in the heterocyclic ring. Heterocyclic amines can be
26 saturated or unsaturated and can contain various substituents such as nitro,
27 alkoxy, alkyl mercapto, alkyl, alkenyl, aryl, alkaryl, or aralkyl substituents. Generally,
28 the total number of carbon atoms in the substituents will not exceed about 20.
29 Heterocyclic amines can contain heteroatoms other than nitrogen, especially
30 oxygen and sulfur. The 5- and 6-membered heterocyclic rings are preferred.

31

32 Among the suitable heterocyclics are aziridines, azetidines, azolidines, tetra- and
33 di-hydro pyridines, pyrroles, indoles, piperadines, isoindoles, morpholines,

1 thiomorpholines, N-aminoalkyl-morpholines, N-aminoalkylthiomorpholines,
2 azepines, and tetra-, di- and perhydroderivatives of each of the above and mixtures
3 of two or more of these heterocyclic amines. Preferred heterocyclic amines are the
4 saturated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen
5 and/or sulfur in the hetero ring, especially the piperidines, thiomorpholines,
6 morpholines, pyrrolidines, and the like. Piperidine, aminoalkyl-substituted
7 piperidines, morpholine, aminoalkyl-substituted morpholines, pyrrolidine, and
8 aminoalkyl-substituted pyrrolidines, are useful.

9
10 Examples of useful tertiary amines include trimethyl amine, triethyl amine, tripropyl
11 amine, tributyl amine, monomethyldiethyl amine, monoethyldimethyl amine,
12 dimethylpropyl amine, dimethylbutyl amine, dimethylpentyl amine, dimethylhexyl
13 amine, dimethylheptyl amine, dimethyloctyl amine, dimethylnonyl amine,
14 dimethyldecyl amine, dimethyldicodanyl amine, dimethylphenyl amine, N,N-dioctyl-
15 1-octanamine, N,N-didodecyl-1-dodecanamine tricoco amine, trihydrogenated-
16 tallow amine, N-methyl-dihydrogenated tallow amine, N,N-dimethyl-1-
17 dodecanamine, N,N-dimethyl-1-tetradecanamine, N,N-dimethyl-1-
18 hexadecanamine, N,N-dimethyl-1-octadecanamine, N,N-dimethylcoco, amine, N,N-
19 dimethyl soyaamine, N,N-dimethyl hydrogenated tallow amine, etc.

20
21 Hydroxyamines analogous to those mono-amines described herein are also useful.
22 The hydroxy-substituted amines contemplated are those having hydroxy
23 substituents bonded directly to a carbon atom other than a carbonyl carbon atom;
24 that is, they have hydroxy groups capable of functioning as alcohols. The
25 hydroxyamines can be primary, secondary or tertiary amines, with the secondary
26 and tertiary amines being preferred, and the tertiary amines being especially
27 preferred. The terms "hydroxyamine" and "aminoalcohol" describe the same class
28 of compounds and, therefore, can be used interchangeably.

29
30 The hydroxyamines include N-(hydroxyl-substituted hydrocarbyl) amines, hydroxyl-
31 substituted poly(hydrocarbyloxy) analogs thereof and mixtures thereof.

1 Examples of the N-(hydroxyl-substituted hydrocarbyl) amines include di- and
2 triethanolamine, dimethylethanolamine, diethylethanolamine, di-(3-hydroxylpropyl)
3 amine, N-(3-hydroxylbutyl) amine, N-(4-hydroxylbutyl) amine, N,N-di-(2-
4 hydroxylpropyl) amine, N-(2-hydroxylethyl) morpholine and its thio analog, N-(2-
5 hydroxylethyl) cyclohexylamine, N-3-hydroxyl cyclopentylamine, o-, m- and p-
6 aminophenol.

7
8 The hydroxyamines can also be ether N-(hydroxy-substituted hydrocarbyl)amines.
9 These are hydroxyl-substituted poly(hydrocarbyloxy) analogs of the above-
10 described hydroxy amines (these analogs also include hydroxyl-substituted
11 oxyalkylene analogs). Such N-(hydroxyl-substituted hydrocarbyl) amines can be
12 conveniently prepared by reaction of epoxides with afore-described amines.

13 The high molecular weight hydrocarbyl monoamines which can be used as amines
14 in this invention are generally prepared by reacting a chlorinated polyolefin having a
15 molecular weight of at least about 400 with ammonia or an amine. The amines that
16 can be used are known in the art and described, for example, in U.S. Pat. Nos.
17 3,275,554 and 3,438,757, both of which are incorporated herein by reference.
18 These amines must possess at least one primary or secondary amino group.

19 A useful method for making the emulsions of the present invention comprises the
20 steps of (1) mixing water, oxygen-supplying component (e.g., ammonium nitrate) in
21 a first premix, (2) mixing the carbonaceous fuel, the emulsifier of the invention in a
22 second premix and (3) adding the first premix to the second premix in any suitable
23 mixing apparatus to form a water-in-oil emulsion. The first premix can be heated
24 until all of the oxygen-supplying component is completely dissolved and the
25 solution may be filtered in order to remove any insoluble residue. The second
26 premix can also be heated to liquefy the ingredients. Any apparatus capable of
27 either low or high shear mixing can be used to prepare the water-in-oil emulsion.

28 The water-in-oil emulsions of this invention can also be made by adding the second
29 premix liquefied organic solution phase to the first premix hot aqueous solution
30 phase with sufficient stirring to invert the phases. However, this method usually

1 requires substantially more energy to obtain the desired dispersion than does the
2 preferred reverse procedure. Alternatively, the water-in-oil emulsions are
3 particularly adaptable to preparation by a continuous mixing process where the two
4 separately prepared liquid phases are pumped through a mixing device wherein
5 they are combined and emulsified.

6 7 **EXAMPLES**

8
9 The invention will be further illustrated by the following examples, which set forth
10 particularly advantageous method embodiments. While the Examples are provided
11 to illustrate the present invention, they are not intended to limit it.

12 Example 1

13 Preparation of PolyPIBSA

14 PolyPIBSA was prepared using the following procedure. To a 12L three neck flask
15 equipped with a heating mantle, temperature probe, nitrogen inlet tube, and an
16 addition funnel, was added at 110°C 5068g (2.197 mol) Glissopal 2300 (high
17 methylvinylidene polybutene from BASF; $M_n = 2300$), and 215.2g maleic anhydride
18 (2.195 mol). The polyisobutene/maleic anhydride charge mole ratio ("CMR") was
19 1.0. To this was added over 2 hours a total of 16.1g di-tert-butylperoxide (0.11
20 mol) dropwise with stirring. The di-tert-butylperoxide/polyisobutene CMR was 0.05.
21 The temperature of the reaction was increased to 170°C over one hour time period
22 as the peroxide addition began. This was then heated overnight at 170°C and then
23 unreacted maleic anhydride was distilled under vacuum. The product was then
24 filtered. The polyPIBSA product had a SAP number of 26.2 mg KOH/g sample,
25 and contained 53.1 % actives. The apparent succinic ratio was 1.06.

26 The "succinic ratio" refers to the ratio calculated in accordance with the procedure
27 and mathematical equation set forth in columns 5 and 6 of U. S. Patent No.
28 5,334,321, issued August 2, 1994 to Harrison and Ruhe, which is hereby
29 incorporated by reference in its entirety. Normally, the term apparent succinic
30 ratio refers to the number of succinic groups per polybutene tail. However, in the
31 context of this application the apparent succinic ratio has a different meaning

depending on the structure of the mixture. For a sample of polyPIBSA (case no. 1), the apparent succinic ratio refers to the ratio of succinic anhydride to polybutene tails that are present in the copolymer. For acid catalyzed thermal PIBSA (case no. 2), the apparent succinic ratio refers to the ratio of the succinic anhydride in the PIBSA plus the succinic anhydrides in the soluble resin to the polybutene tails in the PIBSA. For a mixture of polyPIBSA and acid catalyzed thermal PIBSA, the apparent succinic ratio refers to a combination of case no.1 and case no. 2 above.

Examples 2-5

Other preparations of polyPIBSA were carried out using the procedure of Example 1 with different temperatures and dicumylperoxide (DCP) instead of di-tert-butylperoxide (DTBP). These are reported in Table 1.

Table 1
Preparation of polyPIBSA samples

Example	Peroxide	Temp., °C	Saponification No., mgKOH/g sample	% Actives	Apparent Succinic Ratio
1	DTBP	170	26.2	53.1	1.06
2	DTBP	170	27.3	55.2	1.06
3	DCP	160	Na	60.8	Na
4	DCP	160	Na	60.4	Na
5	DCP	160	29.7	59.3	1.07

Example 6

Preparation of polyPIBSA/sulfonic acid catalyzed thermal PIBSA mixture

To 2800g of the polyPIBSA mixture prepared in Example 1, heated to 232°C and pressurized to 24.7 psia with nitrogen, was added 308g maleic anhydride over 30 minutes. Then to this was added 0.7g alkylbenzene sulfonic acid. The amount of sulfonic acid added relative to the amount of polyisobutene was about 250 ppm. This was then heated for four hours at 232°C at 24.7 psia. Then vacuum was applied to the reactor and the excess maleic anhydride was distilled. The product, which had crude sediment of 1.5 wt.%, was then filtered. The polyPIBSA/PIBSA mixture had a SAP number of 71.0mg KOH/g sample, and 89.0 % actives. The calculated apparent succinic ratio was 1.76.

1

2

Example 7

3

Preparation of polyPIBSA/sulfonic acid catalyzed thermal PIBSA mixture

4

5

To 4840g of the polyPIBSA mixture prepared in Example 5 was added 519g maleic anhydride, and 1.4g alkylbenzene sulfonic acid as in Example 6. The amount of sulfonic acid added relative to the amount of polyisobutene was about 250 ppm.

8

The same temperature, pressure and time were used as in Example 6. After

9

distillation of the excess maleic anhydride, and filtration of the product a

10

polyPIBSA/PIBSA mixture was obtained that had a SAP number of 62.9 mg KOH/g

11

sample and 91.1 % actives. The calculated apparent succinic ratio was 1.51.

12

The following examples describe the preparation of succinimides made from the

13

polyPIBSA/sulfonic acid-catalyzed thermal PIBSA mixture.

14

15

Example 8

16

Preparation of the bis heavy polyamine derivative of the polyPIBSA/sulfonic acid-catalyzed thermal PIBSA

17

18

19

To 225.70g of the polyPIBSA/PIBSA mixture from Example 6 (0.143 mol) was

20

added at 130°C 19.63g HPA (0.0714 mol, a heavy polyamine $M_n=275$, which

21

contains about 6.5 nitrogen atoms per mole), and 276.48g diluent oil. The

22

amine/anhydride CMR was 0.5. This was heated to 165°C. After heating for 72

23

hours, the reaction was cooled. The product had 1.26 %N, a Total Base Number

24

("TBN") of 26.1 mgKOH/g sample, a Total Acid Number ("TAN") of 0.83 mgKOH/g

25

sample, and a viscosity @100°C of 150.5 cSt.

Example 9

Preparation of other succinimides

The procedure of Example 8 was followed except that TETA was used instead of HPA. The chemical and physical properties for this product is included in Table 2.

Table 2

Preparation of polyPIBSA/PIBSA succinimides.

Example	PolyPIBSA/PIBSA example	CMR	Amine	%N	TBN	TAN	Viscosity @ 100°C
8	6	0.5	HPA	1.26	26.1	0.83	150.5
9	6	0.5	TETA	0.755	11.5	1.68	146

The following examples describe the preparation of ethylene carbonate post treated dispersants.

Example 10

Ethylene carbonate post treatment of polyPIBSA/PIBSA succinimides

The polyPIBSA/PIBSA succinimides were post treated with ethylene carbonate according to the following procedure. To a three neck flask equipped with a stirrer, heating mantle, and a nitrogen inlet tube, was added 202.23g of the polyPIBSA/PIBSA succinimide from Example 8. This was heated to 165°C and to this was added 22.36g ethylene carbonate. This was heated overnight and then cooled. This product had 1.20%N, 14.9 TBN, <0.05 TAN, and a viscosity @ 100°C of 353 cSt.

1 Example 11

2 Ethylene carbonate post treatment of succinimide from example 9
3 To 220.14g of the succinimide from Example 9 was added 10.44g ethylene
4 carbonate at 165°C with stirring. This was heated overnight and then cooled. This
5 product had 0.732%N, 6.67 TBN, 0.16 TAN, and a viscosity @ 100°C of 175 cSt.
6

7 Example 12

8 Preparation of ethylene carbonate post treated succinimide using HPA
9 To 1049.28g of the polyPIBSA/PIBSA mixture from Example 7 was added 950.72g
10 diluent oil and 80.87 g HPA (0.294 mol) at 130°C. The amine/PIBSA ratio was 0.5.
11 This was heated with stirring to 165°C overnight. Then to this was added 247.59g
12 ethylene carbonate (2.81 mol). The ethylene carbonate/basic nitrogen CMR was
13 2.0. This was heated at 170°C for 6 hours. This product had 1.23 %N, 0.08 TAN,
14 16.7 TBN, and had a viscosity @ 100°C of 753 cSt.
15

16 Example 13

17 Preparation of ethylene carbonate post treated succinimide using HPA
18 To 47,862g polyPIBSA/PIBSA mixture which had a SAP number of 32.2 mg
19 KOH/g sample, (13.73 mol) was added 1888g HPA (6.87 mol) at 120° C with
20 stirring. The amine/PIBSA CMR was 0.5. This was heated at 165° C for 6 hours.
21 Then to this was added 5775g ethylene carbonate (65.6 mol). The ethylene
22 carbonate/basic nitrogen CMR was 2.0. This was heated at 165° C overnight. The
23 resulting product (52,988g) had 1.22%N, 16.1 TBN and viscosity @ 100°C of 732
24 cSt.

25 The succinimides can be "end-capped" by reacting terminal reactive amines from
26 the polyamine with an endcapping agent. This can be accomplished by adding the
27 end capping agent to the succinimide under reactive conditions, or by adding the
28 endcapping agent to the polyPIBSA, followed by addition of the polyamine, also
29 under reactive conditions. Examples of end capping agents include low molecular
30 weight alkyl succinic anhydrides. Preferably, the alkyl chain is relatively short,
31 which helps maintain a high percent nitrogen in the endcapped product. Conditions

1 for the end capping reaction are typically similar to those employed in the imidation
2 of the polyPIBSA.

3 The following examples describe the preparation of the C₁₂ end capped
4 succinimides.

5

6

Example 14

7

Preparation of the C₁₂ end capped HPA succinimide

8 To 207.15g of polyPIBSA/PIBSA mixture from Example 6 (0.131 mol) was added
9 15.8g tetrapropenylsuccinic anhydride (TPSA; 0.0563 mol) and 253.77g diluent oil.
10 This was stirred at 100°C for 1 hour. The polyPIBSA/PIBSA: TPSA ratio was
11 70/30. To this was added 25.8g HPA (0.0938 mol) and then the reaction
12 temperature was increased to 165°C. This was heated overnight. The product
13 was then cooled. The resulting product had 1.72 %N, 36.4 TBN, 0.75 TAN, and
14 had a viscosity @ 100°C of 136 cSt.

15

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Example 15

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Ethylene carbonate post treatment of succinimide from Example 14

18

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To 197.77g of the succinimide from Example 14 was added at 165°C, 29.85g
ethylene carbonate (0.34 mol). This was heated overnight at 165°C. The resulting
product had 1.59%N, TBN of 21.1, a TAN of <0.05, and a viscosity @ 100°C of 473
cSt.

Example 16

Preparation of EC post treated C₁₂ end capped HPA succinimide

To 632.23g polyPIBSA/PIBSA mixture which had a SAP number of 60.5 mg KOH/g sample, was added 1617g diluent oil. To this was then added 95.6 g TPSA (SAP number 400 mg KOH/g sample, 0.34 mol). The polyPIBSA/PIBSA:TPSA CMR was 1.0. To this was then added HPA 93.73g (0.34 mol). The amine/PIBSA CMR was 1.0. This was heated at 170°C for 6 hours and then cooled. To the resulting product was then added at 100°C, 286.98g ethylene carbonate (3.26 mol). This was heated to 170°C for 7 hours. The EC/basic nitrogen CMR was 2.0. The product from this reaction contained 1.15%N, 15.9 TBN, 0.15 TAN, and had a viscosity @ 100°C of 86.1 cSt.

Example 17

Preparation of EC post treated C₁₂ end capped HPA succinimide

To 42,043g polyPIBSA/PIBSA mixture which had a SAP number of 21.0 mg KOH/g sample (7.87 mol) was added 2166 mol TPSA (7.83 mol) and this was heated to 165°C. To this was added with stirring 2154g HPA (7.83 mol). This was heated for 6 hours. To this was then added 6589g ethylene carbonate (74.88 mol). This was heated at 165-170°C overnight. This product (48,746g) had 1.52 %N, 19.1 TBN, and had a viscosity @100°C of 155.1 cSt.

PERFORMANCE TESTING

The soot thickening test was used to determine the relative performance of the new dispersant variants. Details of the soot thickening test are included in US 5,821,205. The results from the soot thickening test are included in Table 3.

Table 3

Soot thickening test data for new dispersants

Example	Amine	EC/basic N CMR	polyPIBSA/PIBSA:TPS A ratio	% viscosity increase
8	HPA	0	-	86
9	TETA	0	-	174
10	HPA	2	-	24
11	TETA	2	-	46
14	HPA	0	70/30	48
15	HPA	2	70/30	20

The data in Table 3 shows that for the soot thickening tests HPA gives better performance than TETA. Also the EC post-treated materials give better performance than the non-EC treated samples.

1 What is claimed is:

- 2 1. A process for preparing a mixture of (1) a copolymer of a polyalkene and an
3 unsaturated acidic reagent and (2) a polyalkenyl derivative of an unsaturated
4 acidic reagent, said process comprising
5 (a) copolymerizing (1) a polyalkene containing alkylvinylidene isomer and
6 non-alkylvinylidene isomers and (2) an unsaturated acidic reagent under
7 polymerization conditions in the presence of a free radical initiator; and
8 (b) reacting the product of step (a) with an unsaturated acidic reagent at
9 elevated temperature in the presence of a strong acid.
- 10 2. A process according to Claim 1 wherein said polyalkene is a polybutene.
- 11 3. A process according to Claim 2 wherein said polybutene is a polyisobutene.
- 12 4. A process according to Claim 3 wherein at least 50% of said polyisobutene
13 has methylvinylidene end groups.
- 14 5. A process according to Claim 1 wherein said polyalkene has a Mn of from 500
15 to 2500.
- 16 6. A process according to Claim 1 wherein said unsaturated acidic reagent is
17 maleic anhydride.
- 18 7. A process according to Claim 1 wherein said strong acid is a sulfonic acid.
- 19 8. A process according to Claim 7 wherein said sulfonic acid is an alkyl aryl
20 sulfonic acid.
- 21 9. A process according to Claim 8 wherein said alkyl group of said alkyl aryl
22 sulfonic acid has from 4 to 30 carbon atoms.

10. A process according to Claim 7 wherein the sulfonic acid is present in an amount in the range of from 0.0025% to 1.0% based on the total weight of polyalkene.
11. The product produced by a process comprising:
- 5 (a) copolymerizing (1) a polyalkene containing alkylvinylidene isomer and non-alkylvinylidene isomers and (2) an unsaturated acidic reagent under polymerization conditions in the presence of a free radical initiator; and
- (b) reacting the product of step (a) with an unsaturated acidic reagent at elevated temperature in the presence of a strong acid.
- 10 12. A composition comprising a mixture of (1) a copolymer of a polyalkene and an unsaturated acidic reagent and (2) a polyalkenyl derivative of an unsaturated acidic reagent wherein the weight ratio of copolymer to polyalkenyl derivative is about 0.1-10, and wherein the copolymer and the polyalkenyl derivative are prepared using the process of claim 1.
- 15 13. The composition of claim 12 wherein the weight ratio of copolymer to polyalkenyl derivative is about 0.2-5.0.
14. The composition of claim 12 wherein the weight ratio of copolymer to polyalkenyl derivative is about 1-2.
15. A polysuccinimide prepared by reacting a mixture according to claim 12 with
- 20 an amine, a polyamine having at least two basic nitrogens, or mixtures thereof.
16. A concentrate comprising 10 to 90 weight percent of a polysuccinimide of claim 15 and from 90 to 10 weight percent of an organic diluent.
17. A lubricating oil composition comprising a major amount of an oil of lubricating
- 25 viscosity and a minor amount of a polysuccinimide of claim 15.
18. A post-treated composition prepared by treating a polysuccinimide of claim 15 under reactive conditions with a cyclic carbonate.

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- 1 19. The post-treated composition of claim 18 wherein the cyclic carbonate is
2 ethylene carbonate.
- 3 20. A post-treated composition prepared by treating a polysuccinimide of claim 15
4 under reactive conditions with a boron compound.
- 5 21. The post-treated composition of claim 18 wherein the boron compound is
6 boric acid.
- 7 22. A lubricating oil composition comprising a major amount of an oil of lubricating
8 viscosity and a minor amount of the post-treated composition of claim 18.
- 9 23. A concentrate comprising 10 to 90 weight percent of a post-treated
10 composition of claim 18 and from 90 to 10 weight percent of an organic
11 diluent.
- 12 24. A fuel composition comprising a hydrocarbon boiling in the gasoline or diesel
13 range and from about 10 to about 10,000 parts per million of post-treated
14 composition of claim 18.
- 15 25. A fuel concentrate comprising an inert, stable oleophilic solvent boiling in the
16 range of 150-400°F and at least 5 percent by weight of the post-treated
17 composition of claim 18.
- 18 26. A polyester prepared by reacting a mixture according to claim 12 with a polyol.
- 19 27. A concentrate comprising 10 to 90 weight percent of a polyester of claim 26
20 and from 90 to 10 weight percent of an organic diluent.
- 21 28. A lubricating oil composition comprising a major amount of an oil of lubricating
22 viscosity and a minor amount of a polyester of claim 26.
- 23 29. A post-treated composition prepared by treating a polyester of claim 26 under
24 reactive conditions with a boron compound.

1 30. The post-treated composition of claim 29 wherein the boron compound is
2 boric acid.

3 31. A water-in-oil emulsion comprising a discontinuous aqueous phase comprising
4 at least one oxygen-supplying component, a continuous organic phase
5 comprising at least one carbonaceous fuel, and a minor emulsifying amount of
6 at least one emulsifier comprising the product produced by a process
7 comprising (a) copolymerizing (1) a polyalkene containing alkylvinylidene
8 isomer and non-alkylvinylidene isomers and (2) an unsaturated acidic reagent
9 under polymerization conditions in the presence of a free radical initiator, (b)
10 reacting the product of step (a) with an unsaturated acidic reagent at elevated
11 temperature in the presence of a strong acid, and (c) reacting the product of
12 step (b) with ammonia or at least one amine.