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Declarations under Rule 4.17:
— *as to the identity of the inventor (Rule 4.17(i))*
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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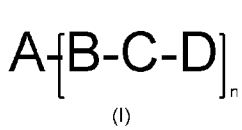
(54) Title: LOW MOLECULAR WEIGHT POLYMERIC SOOT DISPERSANT



(I)

(57) Abstract: A low molecular weight polymeric dispersant composition is described. The polymeric dispersant is represented by the generalized structure: (I) where A is liquid hydrocarbon polymer, B is alkyl imide or alkyl amide, C is polyamine, alkyl amine, alkyl ether amine or alkyl hydroxyl amine, and D is 1-(arene-2-yloxy)propan-2-ol; and n is 1 to 15.

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LOW MOLECULAR WEIGHT POLYMERIC SOOT DISPERSANT

FIELD OF THE DISCLOSURE

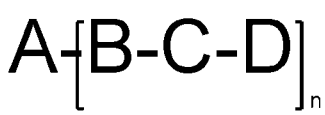
[1] The present disclosure relates to lubricant additives and lubricating oil compositions containing the same. More particularly, the present disclosure relates to low molecular weight polymeric dispersants that can improve wear and/or soot dispersion when used as lubricant additives.

BACKGROUND

[2] Internal combustion engines can produce soot as a result of incomplete combustion. Soot formation is generally more prevalent in diesel engines compared to gasoline engines due to the differences in how fuel is injected and ignited. Accumulation of soot can lead to number of issues such as increasing engine wear leading to engine failure. Thus, improving dispersancy of suspended soot or sludge that forms during the operation or use of the lubricant in engines is critically important for sustained engine operation.

SUMMARY OF THE INVENTION

[3] In one aspect, this disclosure is related to a low molecular weight polymeric dispersant composition, wherein the polymeric dispersant is represented by the following generalized structure:



wherein A is liquid hydrocarbon polymer, B is alkyl imide or alkyl amide, C is polyamine, alkyl amine, alkyl ether amine or alkyl hydroxyl amine, and D is 1-(arene-2-yloxy)propan-2-ol; and n is 1 to 15.

[4] In another aspect, this disclosure is related to a lubricating oil composition comprising: a major amount of a base oil of lubricating viscosity; and a low molecular weight polymeric dispersant represented by the following generalized structure:

$$A\text{-}[B\text{-}C\text{-}D]_n$$

wherein A is liquid hydrocarbon polymer, B is alkyl imide or alkyl amide, C is polyamine, alkyl amine, alkyl ether amine or alkyl hydroxyl amine, and D is 1-(arene-2-yloxy)propan-2-ol; and n is 1 to 15.

[5] In yet another aspect, this disclosure is related to a method for improving wear or soot dispersion in an internal combustion engine, the method comprising lubricating the engine with a lubricating oil composition comprising: a major amount of a base oil of lubricating viscosity; and a low molecular weight polymeric dispersant represented by the following generalized structure:

$$A\text{-}[B\text{-}C\text{-}D]_n$$

wherein A is liquid hydrocarbon polymer, B is alkyl imide or alkyl amide, C is polyamine, alkyl amine, alkyl ether amine or alkyl hydroxyl amine, and D is 1-(arene-2-yloxy)propan-2-ol; and n is 1 to 15.

DETAILED DESCRIPTION

Definitions

[6] The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

[7] The term “a major amount” of a base oil refers to where the amount of the base oil is at least 40 wt. % of the lubricating oil composition. In some embodiments, “a major amount” of a base oil refers to an amount of the base oil more than 50 wt. %, more than 60 wt. %, more than 70 wt. %, more than 80 wt. %, or more than 90 wt. % of the lubricating oil composition.

[8] The term "Total Base Number" or "TBN" refers to the level of alkalinity in an oil sample, which indicates the ability of the composition to continue to neutralize corrosive acids, in accordance with ASTM Standard No. D2896 or equivalent procedure. The test measures the change in electrical conductivity, and the results are expressed as mgKOH/g (the equivalent number of milligrams of KOH needed to neutralize 1 gram of a product). Therefore, a high TBN reflects strongly overbased products and, as a result, a higher base reserve for neutralizing acids.

[9] “HOB” refers to high overbased with a TBN above 250 on an actives basis and “LOB” refers to low overbased with a TBN below 100 on an actives basis.

[10] The term “liquid polymer” and/or related terms such as “liquid hydrocarbon polymer” refers to a polymer that is liquid under ambient temperature and pressure. In some embodiments, the liquid polymers of the present disclosure exhibit KV100 of less than 3000 cSt and can be chemically grafted (e.g., radical initiation, acylating agent, etc.). Specific examples of liquid hydrocarbon polymers include “liquid olefin copolymer” which refers to an olefin copolymer that is liquid under ambient temperature and pressure.

Description

[11] This disclosure relates to a low molecular weight polymeric dispersants and lubricating oil compositions containing the same. The low molecular weight polymeric dispersant can be used as a lubricant additive to impart one or more performance benefits to a lubricating oil composition.

Polymeric Dispersant

[12] The low molecular weight polymeric dispersant can be used as a lubricant additive to provide protection against wear and/or improve soot dispersion in an internal combustion engine.

[13] In some embodiments, the low molecular weight polymer dispersant can be represented by the following generalized structure:

$$A\text{-}[B\text{-}C\text{-}D]_n$$

wherein A is liquid hydrocarbon polymer; B is independently alkyl imide or alkyl amide; C is independently polyamine, alkyl amine, alkyl ether amine, or alkyl hydroxyl amine; D is 1-(arene-2-yloxy)propan-2-ol; and wherein n is 1 to 15. In some preferred embodiments, n is 3 to 9. The liquid hydrocarbon polymer has average number molecular weight (Mn) of about 1,500 to about 16,000.

[14] The low molecular weight polymeric dispersant of this disclosure may be synthesized or obtained by any compatible means. One synthetic approach involves grafting a low molecular weight polymer with an acylating grafting agent, functionalizing the grafted polymer with a nucleophilic compound (e.g., polyamine), and post-treating with an epoxide (e.g., aryl glycidyl ether). Another approach involves grafting a low molecular weight polymer with an allyl or vinyl aminic grafting agent and post-treating with an epoxide (e.g., aryl glycidyl ether).

[15] In accordance with this disclosure, the low molecular weight polymeric dispersant may be obtained by a series of reaction steps determined by the type of grafting agent used.

[16] In one series of reactions, the low molecular weight polymeric dispersant can be obtained by i) grafting a liquid hydrocarbon polymer with an acylating grafting agent, ii) functionalizing with a polyamine, and iii) post-treating with an aryl glycidyl ether.

[17] In another series of reactions, the low molecular weight polymeric dispersant can be obtained by i) grafting a liquid hydrocarbon polymer with an allyl or vinyl aminic grafting agent and ii) post-treating with an aryl glycidyl ether.

[18] Without being limited by theory, it is believed that the post-treatment step greatly enhances the dispersant properties of the low molecular weight polymeric dispersant.

Reaction Product

[19] In some embodiments, the low molecular weight polymeric dispersant is the reaction product of a liquid hydrocarbon polymer having a number average molecular weight (M_n) from about 1,500 and about 16,000; an acylating grafting agent; a polyamine; and an aryl glycidyl ether.

[20] In some embodiments, the low molecular weight polymeric dispersant is the reaction product of a liquid hydrocarbon polymer having a number average molecular weight (M_n) from about 1,500 and about 16,000; an allyl or vinyl aminic grafting agent; and an aryl glycidyl ether.

[21] During the series of reaction steps leading to the reaction product (i.e., low molecular polymeric dispersant), the aryl glycidyl ether is added during the final reaction step (i.e., as a post-treatment).

[22] The liquid hydrocarbon polymer of this disclosure can be characterized as having a low molecular weight, particularly when compared to olefin copolymers conventionally used as

viscosity index improvers. The Mn of the liquid hydrocarbon polymer can be measured by any compatible method such as gel permeation chromatography.

Number Average Molecular Weight

[23] The number average (Mn) molecular weight of the liquid hydrocarbon polymer is from about 1,500 to about 16,000 such as from about 1,500 to about 15,500, about 1,500 to about 15,000, about 1,500 to about 14,500, about 1,500 to about 14,000, about 1,500 to about 13,500, about 1,500 to about 13,000, about 1,500 to about 12,500, about 1,500 to about 12,000, about 1,500 to about 11,500, about 1,500 to about 11,000, about 1,500 to about 10,500, about 1,500 to about 10,000, about 1,500 to about 9,500, about 1,500 to about 9,000, about 1,500 to about 8,500, about 1,500 to about 8,000, about 1,500 to about 7,500, about 1,500 to about 7,000, about 1,500 to about 6,500, about 1,500 to about 6,000, about 1,500 to about 5,500, about 1,500 to about 5,000, about 1,500 to about 4,500, about 1,500 to about 4,000, about 1,500 to about 3,500, about 1,500 to about 3,000, about 1,500 to about 2,500, about 1,500 to about 2,000, about 2,000 to about 16,000, about 2,000 to about 15,500, about 2,000 to about 15,000, about 2,000 to about 14,500, about 2,000 to about 14,000, about 2,000 to about 13,500, about 2,000 to about 13,000, about 2,000 to about 12,500, about 2,000 to about 12,000, about 2,000 to about 11,500, about 2,000 to about 11,000, about 2,000 to about 10,500, about 2,000 to about 10,000, about 2,000 to about 9,500, about 2,000 to about 9,000 about 2,000 to about 8,500, about 2,000 to about 8,000, about 2,000 to about 7,500, about 2,000 to about 7,000, about 2,000 to about 6,500, about 2,000 to about 6,000, about 2,000 to about 5,500, about 2,000 to about 5,000, about 2,000 to about 4,500, about 2,000 to about 4,000, about 2,000 to about 3,500, about 2,000 to about 3,000, about 2,000 to about 2,500, about 2,500 to about 16,000, about 2,500 to about 15,500, about 2,500 to about 15,000, about 2,500 to about

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[24] Suitable examples of liquid hydrocarbon polymers include, but are not limited to, ethylene-propylene copolymers, ethylene-based polymers, or propylene-based polymers. Ethylene or

propylene-based polymers herein can include blends or reacted products of ethylene or propylene and one or more C4 to C28 alpha-olefins, and additionally optionally other dienes or polyenes and thus may herein also include terpolymers, and other higher forms.

[25] In some embodiments, the ethylene content of the copolymer is in the range of 10 to 80 percent by weight, such as 10 to 75 percent, 10 to 70 percent, 10 to 65 percent, 10 to 60 percent 10 to 50 percent, 10 to 45 percent, 10 to 40 percent, 10 to 35 percent, 10 to 30 percent 10 to 25 percent 10 to 20 percent, 10 to 15 percent, 15 to 80 percent, 15 to 75 percent, 15 to 70 percent, 15 to 65 percent, 15 to 60 percent, 15 to 55 percent, 15 to 50 percent, 15 to 45 percent, 15 to 40 percent, 15 to 35 percent, 15 to 30 percent, 15 to 25 percent, 15 to 20 percent, 20 to 80 percent, 20 to 75 percent, 20 to 70 percent, 20 to 65 percent, 20 to 60 percent, 20 to 55 percent, 20 to 50 percent, 20 to 45 percent, 20 to 40 percent, 20 to 35 percent, 20 to 30 percent, 20 to 25 percent, 25 to 80 percent, 25 to 75 percent, 25 to 70 percent, 25 to 65 percent, 25 to 60 percent, 25 to 55 percent, 25 to 50 percent, 25 to 45 percent, 25 to 40 percent, 25 to 35 percent, 25 to 30 percent, 30 to 80 percent, 30 to 75 percent, 30 to 70 percent, 30 to 65 percent, 30 to 60 percent, 30 to 55 percent, 30 to 50 percent, 30 to 45 percent, 30 to 40 percent, 30 to 35 percent, 35 to 80 percent, 35 to 75 percent, 35 to 70 percent, 35 to 65 percent, 35 to 60 percent, 35 to 55 percent, 35 to 50 percent, 35 to 45 percent, 35 to 40 percent, 40 to 80 percent, 40 to 75 percent, 40 to 70 percent, 40 to 65 percent, 40 to 60 percent, 40 to 55 percent, 40 to 50 percent, 40 to 45 percent, 45 to 80 percent, 45 to 75 percent, 45 to 70 percent, 45 to 65 percent, 45 to 60 percent, 45 to 55 percent, 45 to 50 percent, 50 to 80 percent, 50 to 75 percent, 50 to 70 percent, 50 to 65 percent, 50 to 60 percent, 50 to 55 percent, 55 to 80 percent, 55 to 75 percent, 55 to 70 percent, 55 to 65 percent, 55 to 60 percent, 60 to 80 percent, 60 to 75 percent, 60 to 70 percent, 60 to 65 percent, 65 to 80 percent, 65 to 75 percent, 65 to 70 percent, 70 to 80 percent, 70 to 75 percent, or 75 to 80 percent.

[26] In some embodiments, the ethylene-based copolymer is an ethylene-propylene copolymer. The propylene content of the ethylene-propylene copolymer is in the range of 20 to 90 percent by weight, such as 20 to 85 percent, 20 to 80 percent, 20 to 75 percent, 20 to 70 percent, 20 to 65 percent, 20 to 60 percent 20 to 50 percent, 20 to 45 percent, 20 to 40 percent, 20 to 35 percent, 20 to 30 percent 20 to 25 percent, 25 to 90 percent, 25 to 85 percent, 25 to 80 percent, 25 to 75 percent, 25 to 70 percent, 25 to 65 percent, 25 to 60 percent, 25 to 55 percent, 25 to 50 percent, 25 to 45 percent, 25 to 40 percent, 25 to 35 percent, 25 to 30 percent, 30 to 90 percent, 30 to 85 percent, 30 to 80 percent, 30 to 75 percent, 30 to 70 percent, 30 to 65 percent, 30 to 60 percent, 30 to 55 percent, 30 to 50 percent, 30 to 45 percent, 30 to 40 percent, 30 to 35 percent, 35 to 90 percent, 35 to 85 percent, 35 to 80 percent, 35 to 75 percent, 35 to 70 percent, 35 to 65 percent, 35 to 60 percent, 35 to 55 percent, 35 to 50 percent, 35 to 45 percent, 35 to 40 percent, 40 to 90 percent, 40 to 85 percent, 40 to 80 percent, 40 to 75 percent, 40 to 70 percent, 40 to 65 percent, 40 to 60 percent, 40 to 55 percent, 40 to 50 percent, 40 to 45 percent, 45 to 90 percent, 45 to 85 percent, 45 to 80 percent, 45 to 75 percent, 45 to 70 percent, 45 to 65 percent, 45 to 60 percent, 45 to 55 percent, 45 to 50 percent, 50 to 90 percent, 50 to 85 percent, 50 to 80 percent, 50 to 75 percent, 50 to 70 percent, 50 to 65 percent, 50 to 60 percent, 50 to 55 percent, 55 to 90 percent, 55 to 85 percent, 55 to 80 percent, 55 to 75 percent, 55 to 70 percent, 55 to 65 percent, 55 to 60 percent, 60 to 90 percent, 60 to 85 percent, 60 to 80 percent, 60 to 75 percent, 60 to 70 percent, 60 to 65 percent, 65 to 90 percent, 65 to 85 percent, 65 to 80 percent, 65 to 75 percent, 65 to 70 percent, 70 to 90 percent, 70 to 85 percent, 70 to 80 percent, 70 to 75 percent, 75 to 90 percent, 75 to 85 percent, 75 to 80 percent, 80 to 90 percent, 80 to 85 percent, or 85 to 90 percent.

Free Radical Initiator

[27] The grafting reaction can be catalyzed by a free radical initiator. Examples of free radical initiator include peroxides, hydroperoxides, peresters, and also azo compounds and preferably those which have a boiling point greater than 100°C and decompose thermally within the grafting temperature range to provide free radicals. Representatives of these free-radical initiators are peroxides (diacyl peroxides such as benzoyl peroxide, dialkyl peroxides such as 1,1-bis(tert-butylperoxy)cyclohexane, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 2,2-bis(tert-butylperoxy)butane, dicumylperoxide, tert-butylcumylperoxide, bis(tert-butylperoxyisopropyl)benzene, di-tert-butylperoxide (DTBP), di-tert-amylperoxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)-hexyne), hydroperoxides, peroxyesters such as tert-butyl peroxy benzoate, tert-butylperoxy acetate, O,O-tert-butyl-O-(2-ethylhexyl)monoperoxy carbonate, peroxyketals such as n-butyl 4,4-di-(tert-butylperoxy)valerate and the like. The initiator is typically used in an amount of from about 0.005% and about 1% by weight based on the weight of the reaction mixture solution.

[28] The grafting is preferably carried out in an inert atmosphere, such as under nitrogen blanketing. A more detailed discussion of free radical initiators can be found in Reactive Modifiers for Polymers Softcover reprint of the original 1st ed. 1997 Edition. by S. Al-Malaika (Editor), the relevant parts of which are hereby incorporated by reference.

Grafting Agent

[29] Suitable grafting agents of this disclosure include i) an acylating grafting agent (e.g., ethylenically unsaturated acylating agent) or ii) an allyl or vinyl aminic grafting agent (e.g., allyl amines or vinyl amines). The grafting agents of this disclosure generally feature 2 reaction sites. One reaction site allows the grafting agent to form a chemical linkage with the low molecular

weight hydrocarbon polymer. The second reaction site allows the grafting agent to form a chemical linkage with a polyamine in the case of an acylating grafting agent. When allyl or vinyl aminic grafting agent is used, the second reaction site is available for post-treatment with an aryl glycidyl ether.

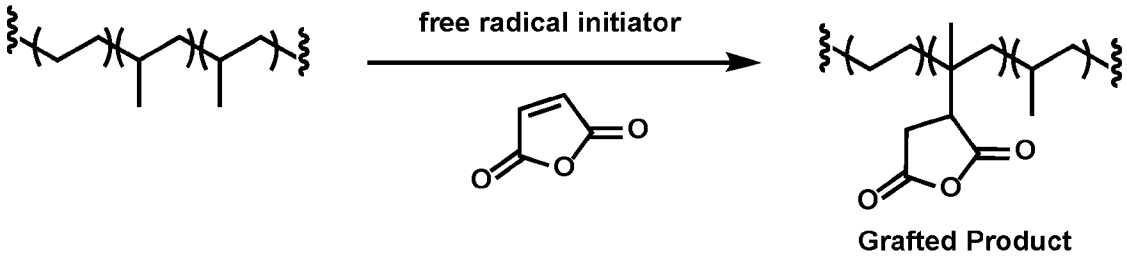
Acylating Grafting Agent

[30] In some embodiments, the acylating grafting agent is an ethylenically unsaturated acylating agent. In some embodiments, the ethylenically unsaturated acylating agent is a carboxylic acid or functional derivative thereof (including esters and anhydrides). The carboxylic acid may include, for example, acrylic acid, crotonic acid, methyacrylic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, chloromaleic acid, aconitic acid, methylcrotonic acid, or sorbic acid. In some embodiments, the acylating agent is an ester of the carboxylic acid. In some embodiments, the acylating agent is an anhydride of the carboxylic acid.

[31] The ethylenically unsaturated carboxylic acid or functional derivative thereof is typically grafted onto the hydrocarbon polymer backbone at about 100°C to about 250°C in the presence of a free radical initiator. In this regard, the hydrocarbon polymer backbone has been suitably reacted with the acylating grafting agent in the range of 0.5 to 10.0 wt % of the acylating grafting agent based upon the total mass of polymer.

Radical Initiation Using Acylating Grafting Agent

A non-limiting example of a radical initiated grafting reaction with an acylating grafting agent (maleic anhydride) is shown below:



Allyl or Vinyl Aminic Grafting Agent

[32] In some embodiments, the grafting agent is allyl or vinyl aminic grafting agent. As alluded to earlier, the allyl or vinyl aminic grafting agent generally includes a first reaction site – an allyl or vinyl group that can react with the polymer and a second reaction site – an amine that can be post-treated by a post-treatment agent such as an aryl glycidyl ether.

[33] The allyl or vinyl aminic graft agent can be represented by the following generalized structure:

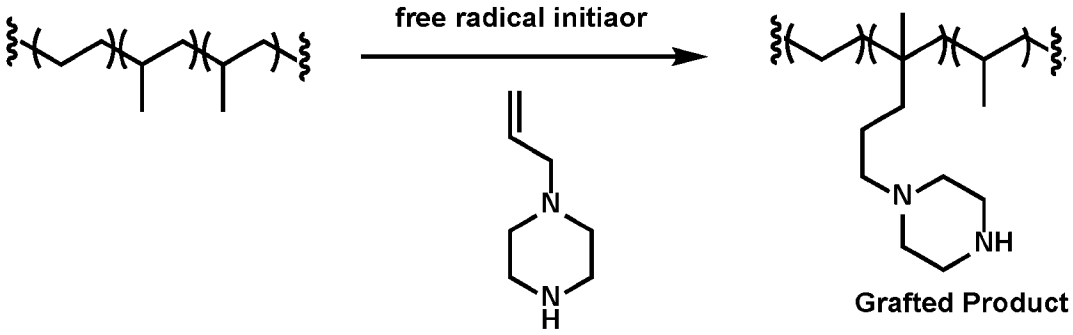
$$W\text{–}Z$$

wherein W is vinyl, alkyl vinyl, allyl, or alkyl allyl group and Z is piperazine, alkylamine, arylamine, formamide, alkyl carbamide, alkyl amide, or aryl amide.

[34] Specific examples of suitable allyl or vinyl aminic grafting agent include, for example, 1-ethenylpiperazine, 1-(prop-1-en-2-yl)piperazine, 1-allylpiperazine, N-allylmethylamine, allylcyclohexylamine, N-allylaniline, N,2-dimethyl-2-propen-1-amine, N-ethyl-2-methylallylamine, 1-(2-methylprop-2-en-1-yl)piperazine, and N-vinylformamide. Specific examples of suitable allyl or vinyl aminic grafting agents that need deprotection reaction before post-treatment with aryl glycidyl ether include, for example, N-vinylacetamide, N-vinylbenzamide, and methyl vinylcarbamate.

Radical Initiation Using Allyl Aminic Grafting Agent

[35] A non-limiting example of a radical initiated grafting reaction with allyl aminic grafting agent (allyl piperazine) is shown below:



Polyamine

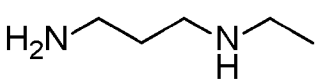
[36] The polyamines of this disclosure can be used to functionalize acylating grafting agents during the synthesis of the low molecular weight polymeric dispersant. The polyamine used in the synthesis of the low molecular weight polymeric dispersant can be represented by the following generalized structure:

$$H_2N–X–Y$$

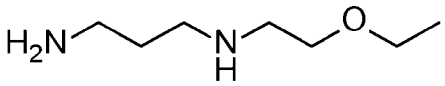
wherein X is C_2-C_{10} hydrocarbyl group, amino alkyl group, ether group, thioether group, or aromatic group and Y is amino C_1-C_{10} hydrocarbyl group, amino alkyl hydroxyl group, amino alkyl ether group, amino alkyl thioether group, amino aromatic group, or piperazine.

[37] Particularly useful polyamines include aminoethylpiperazine, aminoethylethanolamine, and N-phenyl-p-phenylenediamine.

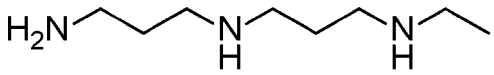
[38] Non-limiting examples of polyamines include the following:



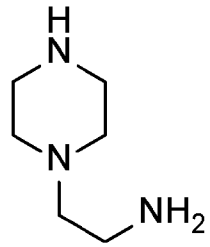
N^1-ethylpropane-1,3-diamine



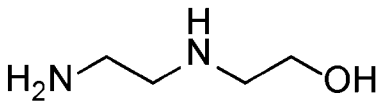
N^1-(2-ethoxyethyl)propane-1,3-diamine



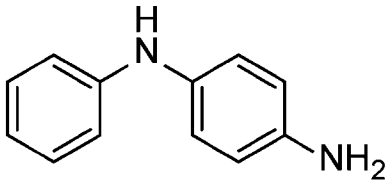
N^1-(3-aminopropyl)-N^3-ethylpropane-1,3-diamine



Aminoethylpiperazine (AEP)



Aminoethylethanolamine (AEEA)



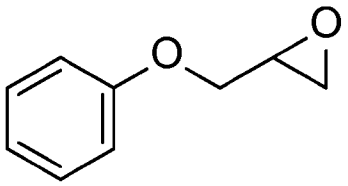
N-phenyl-p-phenylenediamine (NPPDA)

Glycidyl Ethers

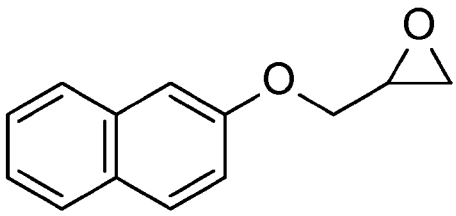
[39] The grafted product (when using allyl or vinyl aminic grafting agent) or the polyamine functionalized grafted product (when using acylating grafting agent) includes a second reaction

site (aminic nitrogen) which allows for post-treatment with a glycidyl ether. Due to its reactivity, secondary nitrogen is generally more desirable than primary or tertiary nitrogen.

[40] Suitable examples of aryl glycidyl ethers include, but are not limited to, phenyl glycidyl ether and naphthyl glycidyl ether.



Phenyl glycidyl ether



2-Naphthyl glycidyl ether

[41] Without being limited by theory, it is believed that post-treatment of the grafted product or polyamine functionalized grafted product can greatly enhance soot dispersing capabilities. It is also believed that the presence of a secondary nitrogen on the grafted product or polyamine functionalized grafted product is highly desirable for post-treatment(s) due to the reactivity of secondary nitrogen compared to primary nitrogen or tertiary nitrogen.

Other Additives

[42] Optionally, the lubricating oil composition may further comprise an additive that can impart or improve any desirable property of the lubricating oil composition. Any additive known to a person of ordinary skill in the art may be used in the lubricating oil compositions disclosed herein. Some suitable additives have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition. London, Springer, (1996); and Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York, Marcel Dekker (2003), both of which are incorporated herein by reference. In some embodiments, the additive can be selected from the

group consisting of antioxidants, antiwear agents, detergents, rust inhibitors, demulsifiers, friction modifiers, multi-functional additives, viscosity index improvers, pour point depressants, foam inhibitors, metal deactivators, dispersants, corrosion inhibitors, lubricity improvers, thermal stability improvers, anti-haze additives, icing inhibitors, dyes, markers, static dissipaters, biocides and combinations thereof.

[43] In general, the concentration of each of the additives in the lubricating oil composition, when used, may range from about 0.001 wt. % to about 10 wt. %, from about 0.01 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 2.5 wt. %, based on the total weight of the lubricating oil composition. Further, the total amount of the additives in the lubricating oil composition may range from about 0.001 wt. % to about 20 wt. %, from about 0.01 wt. % to about 10 wt. %, or from about 0.1 wt. % to about 5 wt. %, based on the total weight of the lubricating oil composition.

Detergents

[44] The lubricating oil composition may comprise a metal detergent such as a metal salicylate, metal phenate, or metal sulfonate. The metal can be any metal suitable for making detergents. Non-limiting examples of suitable metals include alkali metals, alkaline earth metals and transition metals. In some embodiments, the metal is Ca, Mg, Ba, K, Na, Li or the like.

[45] Generally, the amount of the detergent is from about 0.001 wt. % to about 10 wt. %, from about 0.05 wt. % to about 3 wt. %, or from about 0.1 wt. % to about 1 wt. %, based on the total weight of the lubricating oil composition.

[46] Optionally, the lubricating oil composition may comprise additional detergents generally known in the art. Some suitable detergents have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapter 3, pages 75-85 (1996); and

Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York, Marcel Dekker, Chapter 4, pages 113-136 (2003), both of which are incorporated herein by reference. Examples of these detergents include phenates, salicylates, phosphonates, and the like.

[47] In some embodiments the detergent comprises at least one high overbased (TBN above 250 on an actives basis).

[48] Overbased metal detergents are generally produced by carbonating a mixture of hydrocarbons, detergent acid, for example: sulfonic acid, alkylhydroxybenzoate etc., metal oxide or hydroxides (for example calcium oxide or calcium hydroxide) and promoters such as xylene, methanol and water. For example, for preparing an overbased calcium sulfonate, in carbonation, the calcium oxide or hydroxide reacts with the gaseous carbon dioxide to form calcium carbonate. The sulfonic acid is neutralized with an excess of CaO or $Ca(OH)_2$, to form the sulfonate.

[49] Generally speaking, overbased detergents may be low overbased (LOB), e.g., an overbased salt having a TBN below 100 on an actives basis. In one aspect, the TBN of a low overbased salt may be from about 10 to about 100. In another aspect, the TBN of a low overbased salt may be from about 10 to about 80. Overbased detergents may be medium overbased (MOB), e.g., an overbased salt having a TBN from about 100 to about 250 on an actives basis. In one aspect, the TBN of a medium overbased salt may be from about 100 to about 200. In another aspect, the TBN of a medium overbased salt may be from about 125 to about 175. Overbased detergents may be high overbased (HOB), e.g., an overbased salt having a TBN above 250 on an actives basis. In one aspect, the TBN of a high overbased salt may be from about 250 to about 800 on an actives basis.

[50] In some embodiments, the lubricating oil composition comprises low levels of sulfur containing calcium phenates (e.g., about 40 mmol or less of Ca from sulfurized phenates such as

35 mmol or less, 30 mmol or less, 25 mmol or less, 20 mmol or less, 10 mmol or less, 5 mmol or less and 0 mmol).

Anti-wear agents

[51] Optionally, the lubricating oil composition disclosed herein can comprise one or more anti-wear agents. In some embodiments, the lubricating oil composition is free or substantially free of sulfur-containing anti-wear composition.

[52] Anti-wear agents reduce wear of metal parts. Suitable anti-wear agents include dihydrocarbyl dithiophosphate metal salts such as zinc dihydrocarbyl dithiophosphates (ZDDP) of the following structure:

$Zn[S\text{-}P(=S)(OR^1)(OR^2)]_2$

wherein R^1 and R^2 may be the same of different hydrocarbyl radicals having from 1 to 18 (e.g., 2 to 12) carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R^1 and R^2 groups are alkyl groups having from 2 to 8 carbon atoms (e.g., the alkyl radicals may be ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl, n-hexyl, isohexyl, 2-ethylhexyl). In order to obtain oil solubility, the average number of carbon atoms of the mixture of R^1 and R^2 on the molar basis will be at least 4.5. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates. The zinc dialkyl dithiophosphate is a primary, secondary zinc dialkyl dithiophosphate, or a combination thereof. ZDDP may be present at 3 wt. % or less (e.g., 0.1 to 1.5 wt. %, or 0.5 to 1.0 wt %) of the lubricating oil composition.

Dispersants

[53] The lubricating oil composition disclosed herein can further comprise a dispersant. Dispersants maintain in suspension materials resulting from oxidation during engine operation that are insoluble in oil, thus preventing soot or sludge flocculation and precipitation or deposition on metal parts. Dispersants useful herein include nitrogen-containing, ashless (metal-free) dispersants known to effective to reduce formation of deposits upon use in gasoline and diesel engines. Suitable dispersants include hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acid, hydroxyesters of hydrocarbyl-substituted succinic acid, and Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines. Also suitable are condensation products of polyamines and hydrocarbyl-substituted phenyl acids. Mixtures of these dispersants can also be used. More particularly, succinimide-based dispersants include borated succinimides, non-borated succinimides, post-treated succinimides, and the like.

[54] Basic nitrogen-containing ashless dispersants are well-known lubricating oil additives and methods for their preparation are extensively described in the patent literature. Preferred dispersants are the alkenyl succinimides and succinamides where the alkenyl-substituent is a long-chain of preferably greater than 40 carbon atoms. These materials are readily made by reacting a hydrocarbyl-substituted dicarboxylic acid material with a molecule containing amine functionality. Examples of suitable amines are polyamines such as polyalkylene polyamines, hydroxy-substituted polyamines and polyoxyalkylene polyamines. As is known in the art, the dispersants may be post-treated (e.g., with a boronating agent, epoxide, ethylene carbonate, or a cyclic carbonate). Nitrogen-containing ashless (metal-free) dispersants are basic and contribute to the TBN of a lubricating oil composition to which they are added, without introducing additional

sulfated ash. Dispersants may be present at 0.1 to 10 wt. % (e.g., 0.5 to 8, 0.7 to 7, 0.7 to 6, 0.7 to 6, 0.7 to 5, 0.7 to 4 wt. %), based on an actives level, of the lubricating oil composition. Nitrogen from the dispersants is present from greater than 0.0050 to 0.30 wt. % (e.g., greater than 0.0050 to 0.10 wt. %, 0.0050 to 0.080 wt. %, 0.0050 to 0.060 wt. %, 0.0050 to 0.050 wt. %, 0.0050 to 0.040 wt. %, 0.0050 to 0.030 wt. %) based on the weight of the dispersants in the finished oil.

Antioxidants

[55] Optionally, the lubricating oil composition disclosed herein can further comprise an additional antioxidant that can reduce or prevent the oxidation of the base oil. Any antioxidant known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable antioxidants include amine-based antioxidants (e.g., alkyl diphenylamines, phenyl-α-naphthylamine, alkyl or aralkyl substituted phenyl- α-naphthylamine, alkylated p-phenylene diamines, tetramethyl-diaminodiphenylamine and the like), phenolic antioxidants (e.g., 2-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 2,6-di-tert-butyl-p-cresol, 2,6-di-tert-butylphenol, 4,4'-methylenebis-(2,6-di-tert-butylphenol), 4,4'-thiobis(6-di-tert-butyl-o-cresol) and the like), sulfur-based antioxidants (e.g., dilauryl-3,3'-thiodipropionate, sulfurized phenolic antioxidants and the like), phosphorous-based antioxidants (e.g., phosphites and the like), zinc dithiophosphate, oil-soluble copper compounds and combinations thereof. The amount of the antioxidant may vary from about 0.01 wt. % to about 10 wt. %, from about 0.05 wt. % to about 5 wt. %, or from about 0.1 wt. % to about 3 wt. %, based on the total weight of the lubricating oil composition. Some suitable antioxidants have been described in Leslie R. Rudnick, "Lubricant Additives: Chemistry and Applications," New York. Marcel Dekker, Chapter 1, pages 1-28 (2003), which is incorporated herein by reference.

Foam Inhibitors

[56] The lubricating oil composition disclosed herein can optionally comprise a foam inhibitor or an anti-foam that can break up foams in oils. Any foam inhibitor or anti-foam known by a person of ordinary skill in the art may be used in the lubricating oil composition. Non-limiting examples of suitable anti-foams include silicone oils or polydimethylsiloxanes, fluorosilicones, alkoxylated aliphatic acids, polyethers (e.g., polyethylene glycols), branched polyvinyl ethers, alkyl acrylate polymers, alkyl methacrylate polymers, polyalkoxyamines and combinations thereof. In some embodiments, the anti-foam comprises glycerol monostearate, polyglycol palmitate, a trialkyl monothiophosphate, an ester of sulfonated ricinoleic acid, benzoylacetone, methyl salicylate, glycerol monooleate, or glycerol dioleate. The amount of the anti-foam may vary from about 0.0005 wt. % to about 5 wt. %, from about 0.05 wt. % to about 3 wt. %, or from about 0.1 wt. % to about 1 wt. %, based on the total weight of the lubricating oil composition. Some suitable anti-foams have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapter 6, pages 190-193 (1996), which is incorporated herein by reference.

Molybdenum Additive

[57] In some embodiments, the lubricating oil composition comprises a molybdenum additive. Some non-limiting examples of suitable molybdenum additives include molybdenum succinimide, sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organophosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.

The Oil of Lubricating Viscosity

[58] The lubricating oil compositions disclosed herein generally comprise at least one oil of lubricating viscosity. Any base oil known to a skilled artisan can be used as the oil of lubricating viscosity disclosed herein. Some base oils suitable for preparing the lubricating oil compositions have been described in Mortier et al., "Chemistry and Technology of Lubricants," 2nd Edition, London, Springer, Chapters 1 and 2 (1996); and A. Sequeria, Jr., "Lubricant Base Oil and Wax Processing," New York, Marcel Decker, Chapter 6, (1994); and D. V. Brock, Lubrication Engineering, Vol. 43, pages 184-5, (1987), all of which are incorporated herein by reference. Generally, the amount of the base oil in the lubricating oil composition may be from about 70 to about 99.5 wt. %, based on the total weight of the lubricating oil composition. In some embodiments, the amount of the base oil in the lubricating oil composition is from about 75 to about 99 wt. %, from about 80 to about 98.5 wt. %, or from about 80 to about 98 wt. %, based on the total weight of the lubricating oil composition.

[59] In certain embodiments, the base oil is or comprises any natural or synthetic lubricating base oil fraction. Some non-limiting examples of synthetic oils include oils, such as polyalphaolefins or PAOs, prepared from the polymerization of at least one alpha-olefin, such as ethylene, or from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases, such as the Fisher-Tropsch process. In certain embodiments, the base oil comprises less than about 10 wt. % of one or more heavy fractions, based on the total weight of the base oil. A heavy fraction refers to a lube oil fraction having a viscosity of at least about 20 cSt at 100°C. In certain embodiments, the heavy fraction has a viscosity of at least about 25 cSt or at least about 30 cSt at 100° C. In further embodiments, the amount of the one or more heavy fractions in the base oil is

less than about 10 wt. %, less than about 5 wt. %, less than about 2.5 wt. %, less than about 1 wt. %, or less than about 0.1 wt. %, based on the total weight of the base oil. In still further embodiments, the base oil comprises no heavy fraction.

[60] In certain embodiments, the lubricating oil compositions comprise a major amount of a base oil of lubricating viscosity. In some embodiments, the base oil has a kinematic viscosity at 100°C. from about 2.5 centistokes (cSt) to about 20 cSt, from about 4 centistokes (cSt) to about 20 cSt, or from about 5 cSt to about 16 cSt. The kinematic viscosity of the base oils or the lubricating oil compositions disclosed herein can be measured according to ASTM D 445, which is incorporated herein by reference.

[61] In other embodiments, the base oil is or comprises a base stock or blend of base stocks. In further embodiments, the base stocks are manufactured using a variety of different processes including, but not limited to, distillation, solvent refining, hydrogen processing, oligomerization, esterification, and rerefining. In some embodiments, the base stocks comprise a rerefined stock. In further embodiments, the rerefined stock shall be substantially free from materials introduced through manufacturing, contamination, or previous use.

[62] In some embodiments, the base oil comprises one or more of the base stocks in one or more of Groups I-V as specified in the American Petroleum Institute (API) Publication 1509, Fourteen Edition, December 1996 (i.e., API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils), which is incorporated herein by reference. The API guideline defines a base stock as a lubricant component that may be manufactured using a variety of different processes. Groups I, II and III base stocks are mineral oils, each with specific ranges of the amount of saturates, sulfur content and viscosity index. Group IV base stocks are polyalphaolefins (PAO). Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[63] In some embodiments, the base oil comprises one or more of the base stocks in Group I, II, III, IV, V or a combination thereof. In other embodiments, the base oil comprises one or more of the base stocks in Group II, III, IV or a combination thereof. In further embodiments, the base oil comprises one or more of the base stocks in Group II, III, IV or a combination thereof wherein the base oil has a kinematic viscosity from about 2.5 centistokes (cSt) to about 20 cSt, from about 4 cSt to about 20 cSt, or from about 5 cSt to about 16 cSt at 100°C.

[64] The base oil may be selected from the group consisting of natural oils of lubricating viscosity, synthetic oils of lubricating viscosity and mixtures thereof. In some embodiments, the base oil includes base stocks obtained by isomerization of synthetic wax and slack wax, as well as hydrocrackate base stocks produced by hydrocracking (rather than solvent extracting) the aromatic and polar components of the crude. In other embodiments, the base oil of lubricating viscosity includes natural oils, such as animal oils, vegetable oils, mineral oils (e.g., liquid petroleum oils and solvent treated or acid-treated mineral oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types), oils derived from coal or shale, and combinations thereof. Some non-limiting examples of animal oils include bone oil, lanolin, fish oil, lard oil, dolphin oil, seal oil, shark oil, tallow oil, and whale oil. Some non-limiting examples of vegetable 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, and meadow foam oil. Such oils may be partially or fully hydrogenated.

[65] In some embodiments, the synthetic oils of lubricating viscosity include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and inter-polymerized olefins, alkylbenzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, as well as their derivatives, analogues and homologues thereof, and the like. In other embodiments, the synthetic

oils include alkylene oxide polymers, interpolymers, copolymers and derivatives thereof wherein the terminal hydroxyl groups can be modified by esterification, etherification, and the like. In further embodiments, the synthetic oils include the esters of dicarboxylic acids with a variety of alcohols. In certain embodiments, the synthetic oils include esters made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers. In further embodiments, the synthetic oils include tri-alkyl phosphate ester oils, such as tri-n-butyl phosphate and tri-iso-butyl phosphate.

[66] In some embodiments, the synthetic oils of lubricating viscosity include silicon-based oils (such as the polyakyl-, polyaryl-, polyalkoxy-, polyaryloxy-siloxane oils and silicate oils). In other embodiments, the synthetic oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, polyalphaolefins, and the like.

[67] Base oil derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic base oil. Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst.

[68] In further embodiments, the base oil comprises a poly-alpha-olefin (PAO). In general, the poly-alpha-olefins may be derived from an alpha-olefin having from about 2 to about 30, from about 4 to about 20, or from about 6 to about 16 carbon atoms. Non-limiting examples of suitable poly-alpha-olefins include those derived from octene, decene, mixtures thereof, and the like. These poly-alpha-olefins may have a viscosity from about 2 to about 15, from about 3 to about 12, or from about 4 to about 8 centistokes at 100° C. In some instances, the poly-alpha-olefins may be used together with other base oils such as mineral oils.

[69] In further embodiments, the base oil comprises a polyalkylene glycol or a polyalkylene glycol derivative, where the terminal hydroxyl groups of the polyalkylene glycol may be modified

by esterification, etherification, acetylation and the like. Non-limiting examples of suitable polyalkylene glycols include polyethylene glycol, polypropylene glycol, polyisopropylene glycol, and combinations thereof. Non-limiting examples of suitable polyalkylene glycol derivatives include ethers of polyalkylene glycols (e.g., methyl ether of polyisopropylene glycol, diphenyl ether of polyethylene glycol, diethyl ether of polypropylene glycol, etc.), mono- and polycarboxylic esters of polyalkylene glycols, and combinations thereof. In some instances, the polyalkylene glycol or polyalkylene glycol derivative may be used together with other base oils such as poly-alpha-olefins and mineral oils.

[70] In further embodiments, the base oil comprises any of the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, and the like) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, and the like). Non-limiting examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the like.

[71] In further embodiments, the base oil comprises a hydrocarbon prepared by the Fischer-Tropsch process. The Fischer-Tropsch process prepares hydrocarbons from gases containing hydrogen and carbon monoxide using a Fischer-Tropsch catalyst. These hydrocarbons may require further processing in order to be useful as base oils. For example, the hydrocarbons may be dewaxed, hydroisomerized, and/or hydrocracked using processes known to a person of ordinary skill in the art.

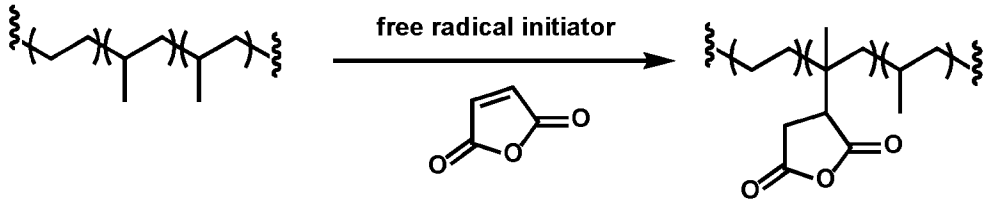
[72] In further embodiments, the base oil comprises an unrefined oil, a refined oil, a rerefined oil, or a mixture thereof. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. Non-limiting examples of unrefined oils include shale oils obtained directly from retorting operations, petroleum oils obtained directly from primary distillation, and ester oils obtained directly from an esterification process and used without further treatment. Refined oils are similar to the unrefined oils except the former have been further treated by one or more purification processes to improve one or more properties. Many such purification processes are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, and the like. Rerefined oils are obtained by applying to refined oils processes similar to those used to obtain refined oils. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally treated by processes directed to removal of spent additives and oil breakdown products.

[73] The following examples are presented to exemplify embodiments but are not intended to limit the application to the specific embodiments set forth. Unless indicated to the contrary, all parts and percentages are by weight. All numerical values are approximate. When numerical ranges are given, it should be understood that embodiments outside the stated ranges may still fall within the scope of the application. Specific details described in each example should not be construed as necessary features.

EXAMPLES

[74] The following examples are intended for illustrative purposes only and do not limit in any way the scope.

Example 1 - Maleation



[75] Ethylene-propylene copolymer (3015.86 g, KV100 ~600 cSt) was transferred into a stirred 4-liter stainless steel reactor equipped with charging lines for maleic anhydride and di-t-amyl peroxide and blanketed with nitrogen. The copolymer was heated to 150°C.

[76] Maleic anhydride (113.04 g) and di-tert-amyl peroxide (16.95 g) were charged at a constant rate simultaneously into the reactor agitation zone over a 2-hour period. After the charging, the reactor was held at temperature for an additional 15 minutes. Reaction was monitored using FT-IR for completeness. The saponification value of the product was measured to be 39.63 mgKOH/g.

Example 2 - Maleation

[77] Ethylene-propylene copolymer (3001.3 g, KV100 ~600 cSt) was transferred into a stirred 4-liter stainless steel reactor equipped with charging lines for maleic anhydride and di-t-amyl peroxide and blanketed with nitrogen. The copolymer was heated to 150°C.

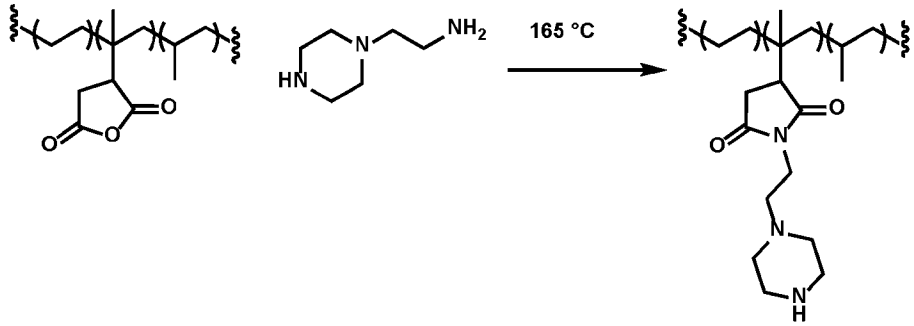
[78] Maleic anhydride (64.38 g) and di-tert-amyl peroxide (4.83 g) were charged at a constant rate simultaneously into the reactor agitation zone over a 2-hour period. After the charging, the reactor was held at temperature for an additional 15 minutes. Reaction was monitored using FT-IR for completeness. The saponification value of the product was measured to be 21.98 mgKOH/g. The maleated ethylene-propylene copolymer has an Mn 4499 based on gel permeation chromatography (calibrated by polystyrene standard) and KV100 was 1035.3 cSt.

Example 3 - Maleation

[79] Ethylene-propylene copolymer (3001.6 g, KV100 ~600 cSt) was transferred into a stirred 4-liter stainless steel reactor equipped with charging lines for maleic anhydride and di-t-amyl peroxide and blanketed with nitrogen. The copolymer was heated to 150°C.

[80] Maleic anhydride (99.23 g) and di-tert-amyl peroxide (7.44 g) were charged at a constant rate simultaneously into the reactor agitation zone over a 2-hour period. After the charging, the reactor was held at temperature for an additional 15 minutes. Reaction was monitored using FT-IR for completeness. 6.23 g alkylated diphenylamine antioxidant was added to quench any remaining free radicals. The reaction mixture was stirred at temperature for another 15 min before concluding the reaction. The saponification value of the product was measured to be 35.01 mgKOH/g. The maleated ethylene-propylene copolymer has an Mn 4258 based on gel permeation chromatography (calibrated by polystyrene standard) and KV100 was 1227.0 cSt.

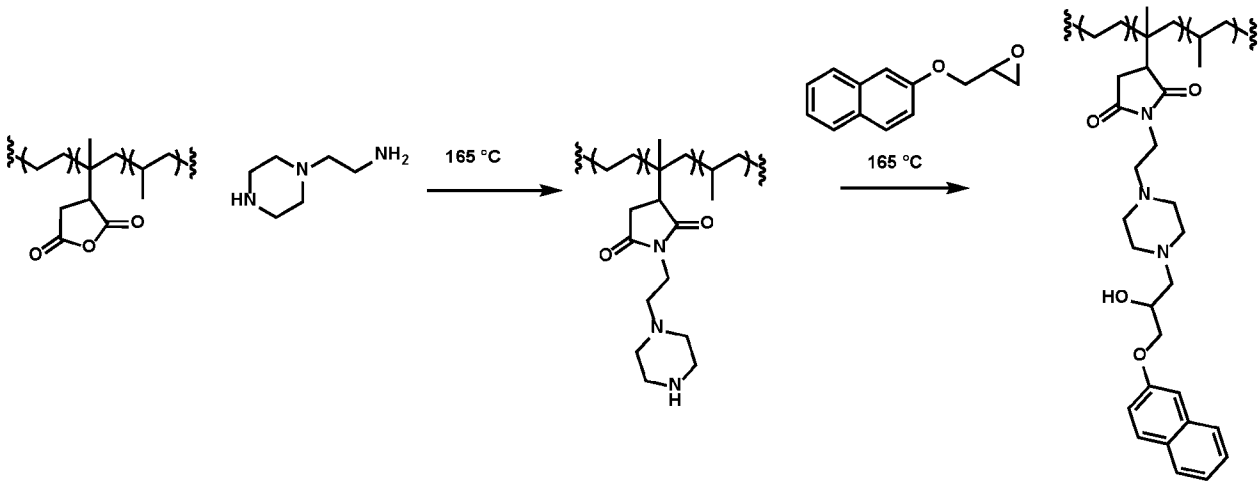
Comparative Example 4 - Imidation



[81] The maleated copolymer prepared in a similar manner as described in Example 1 (237.06 g) and 100 neutral oil (106.6 g) were charged to a stirred 1-liter glass reactor equipped with a condenser and nitrogen sparge. The mixture was heated to 165 ± 5°C with stirring. Aminoethylpiperazine (AEP: 9.97 g; 77.2 mmol) was charged to the reactor. The reaction was held

at 165 ± 5°C for 3 hours with a nitrogen sparge maintained through the hold period to remove generated water. The reaction was monitored using FT-IR for completeness.

Example 5 - Imidation and Post-Treatment



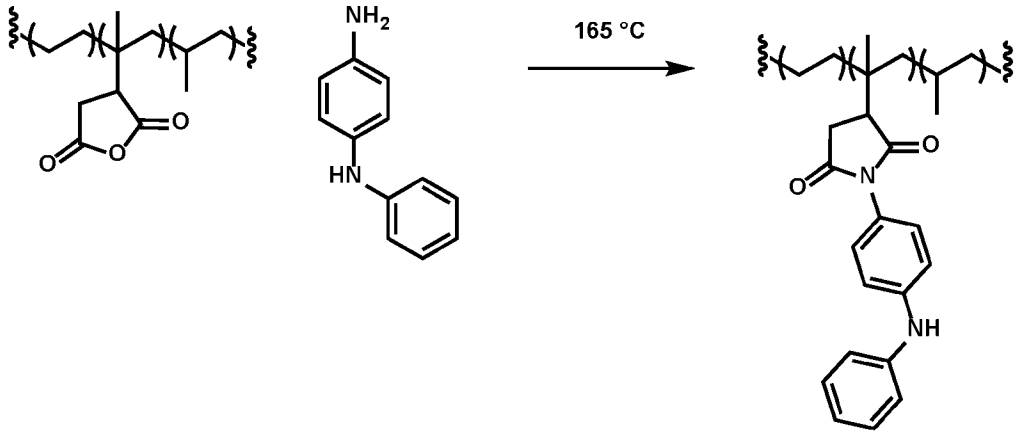
[82] Maleated ethylene-propylene copolymer prepared in a similar manner as described in Example 1 (442.97 g) and 100 neutral oil (220 g) were charged to a stirred 1-liter glass reactor equipped with an overhead condenser and nitrogen sparge. The mixture was heated to 165 ± 5°C while being stirred. Aminoethylpiperazine (AEP: 17.28 g) was charged to the reactor. The reaction was held at 165 ± 5°C for 2 hours. The mixture was sparged using nitrogen to remove water formed during the reaction. Upon completion of the imidation reaction, 2-naphthyl glycidyl ether (NGE: 26.43 g) then added to the reaction mixture. The reaction was held at 165 ± 5°C for 3 hours with a nitrogen sparge to give the final product.

Example 6 - Imidation and Post-Treatment Procedure

[83] Maleated ethylene-propylene copolymer prepared as described in Example 1 (1892.9 g) and 100 neutral oil (523.89 g) were charged to a stirred 4-liter glass reactor equipped with an

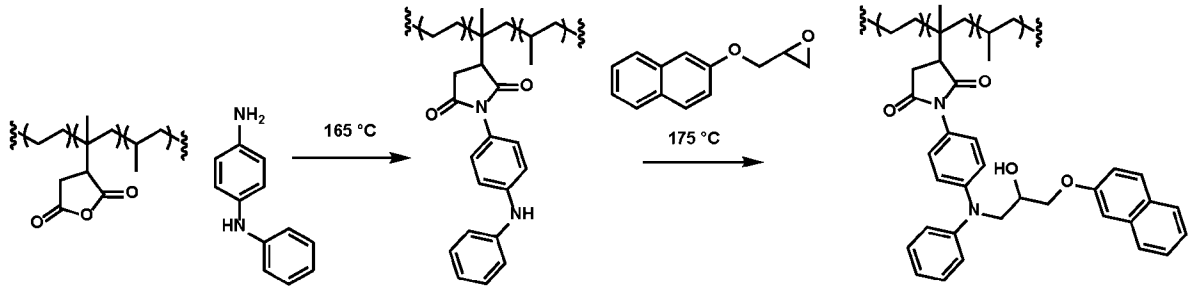
overhead condenser and nitrogen sparge. The mixture was heated to 165 ± 5°C while being stirred. Aminoethylpiperazine (AEP: 79.33 g) was charged to the reactor. The reaction was held at 165 ± 5°C for 2 hours. The mixture was sparged using nitrogen to remove water formed during the reaction. Upon completion of the imidation reaction, 2-naphthyl glycidyl ether (NGE: 123.51 g) was added to the reaction mixture. The reaction was held at 165 ± 5°C for 3 hours with a nitrogen sparge. After completion of the reaction, the contents were diluted with additional mineral oil to achieve a polymer concentration of 55 wt%.

Comparative Example 7 - Imidation Procedure



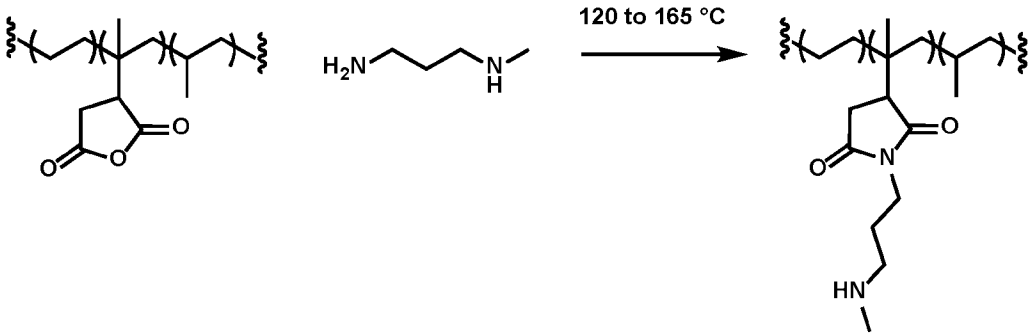
[84] Maleated ethylene-propylene copolymer made as described in Example 2 (514.37 g; saponification value = 21.36 mgKOH/g) was added to a stirred 1-liter glass reactor equipped with overhead condenser and nitrogen purge. The reaction mixture was heated to 165 ± 5°C. N-phenyl-p-phenylenediamine (NPPDA: 18.12 g) was then added and reaction was held for 2 hours. Reaction was monitored via FT-IR for completeness.

Example 8 - Imidation and Post-Treatment Procedure



[85] Maleated ethylene-propylene copolymer made in a similar manner as described in Example 2 (197.1 g; saponification value = 21.94 mgKOH/g) and 100 neutral oil (197.1 g) were added to a stirred glass reactor equipped with a condenser and nitrogen purge. The reactor contents were heated to 130 ± 5°C while being stirred. N-Phenyl-p-phenylenediamine (NPPDA: 7.10 g) was added to the reaction mixture, and the reactor temperature was increased to 165 ± 5°C. The reaction was held for 3 hours to complete the imidation reaction. Upon completion, 2-naphthyl glycidyl ether (NGE: 7.8 g) was added, and the reaction was held at 165 ± 5°C for a total of 7 hours.

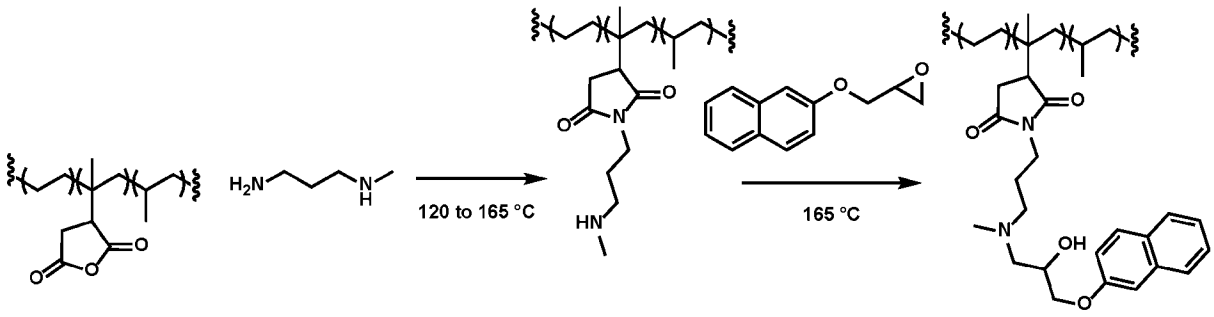
Comparative Example 9 - Imidation



[86] Maleated ethylene-propylene copolymer made in a similar manner as described in Example 3 (200 g; ~3.1wt% maleic anhydride) and 100 neutral oil (178.6 g) were charged to a stirred 1-liter glass reactor equipped with an overhead condenser and nitrogen sparge. The mixture was heated to 100 ± 5°C with stirring. N-Methyl-1,3-propanediamine (MeDAP: 5.57 g) was added to the reactor. The reactor was heated to 120 ± 5°C and held at this temperature for 1 hour with a nitrogen

to remove generated water. The reaction was then heated to 160 ± 5°C and held for 1 hour. The reaction was monitored for completeness via FT-IR.

Example 10 - Imidation and Post-Treatment Procedure



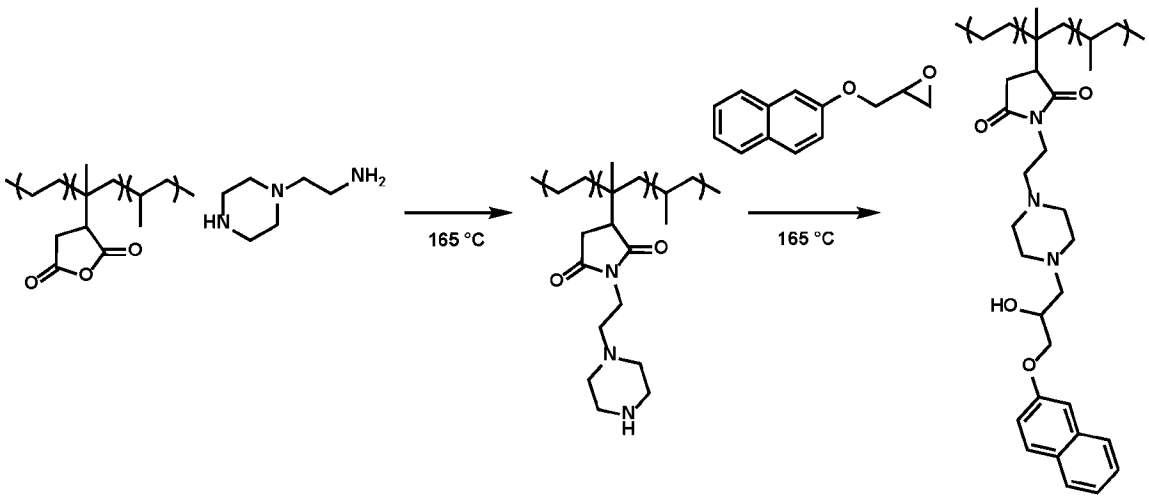
[87] Maleated ethylene-propylene copolymer made in a similar manner as described in Example 3 (200 g; ~3.1wt% maleic anhydride) and 100 neutral oil (178.6 g) were charged to a stirred 1-liter glass reactor equipped with an overhead condenser and nitrogen sparge. The mixture was heated to 100 ± 5°C with stirring. N-Methyl-1,3-propanediamine (MeDAP: 5.57 g) was added to the reactor. The reactor was heated to 120 ± 5°C and held at this temperature for 1 hour with a nitrogen to remove generated water. The reaction was then heated to 160 ± 5°C and held for 1 hour. The reaction was monitored for completeness via FT-IR. Next, 2-naphthyl glycidyl ether (NGE: 12.7 g) was charged to the reactor and the reaction was held at 165 ± 5°C for 1 hour. The reaction was monitored for completeness via FT-IR and ^{1}H-NMR.

Example 11 - Maleation

[88] Ethylene-propylene copolymer (3003.8 g, KV100 ~2000 cSt) was transferred into a stirred 4-liter stainless steel reactor equipped with charging lines for maleic anhydride and di-t-amyl peroxide and blanketed with nitrogen. The copolymer was heated to 170°C.

[89] Maleic anhydride (121.90 g) and di-tert-amyl peroxide (18.29 g) were charged at a constant rate simultaneously into the reactor agitation zone over a 2-hour period. After the charging, the reactor was held at temperature for an additional 15 minutes. The reaction was monitored for completeness via FT-IR. The reaction mixture was stirred at temperature for another 15 min before concluding the reaction. The maleated ethylene-propylene copolymer has an Mn 6916 based on gel permeation chromatography (calibrated by polystyrene standard).

Example 12 - Imidation and Post-Treatment



[90] Maleated ethylene-propylene copolymer from Example 11 (139 g, ~3.9 wt% maleic anhydride), and 100R neutral oil (417 g) were charged to a stirred 4-liter glass reactor equipped with an overhead stirrer, nitrogen sweep, heating mantle, and temperature controller. The mixture was to 165 ± 5°C while being stirred. Aminoethylpiperazine (AEP: 48.74 g) was charged to the reactor. The reaction was held at 165 ± 5°C for 1.5 hours. Upon completion of the imidation reaction, additional 100R neutral oil (394.5 g) was charged to the reactor and the temperature was lowered to 75 ± 5°C.

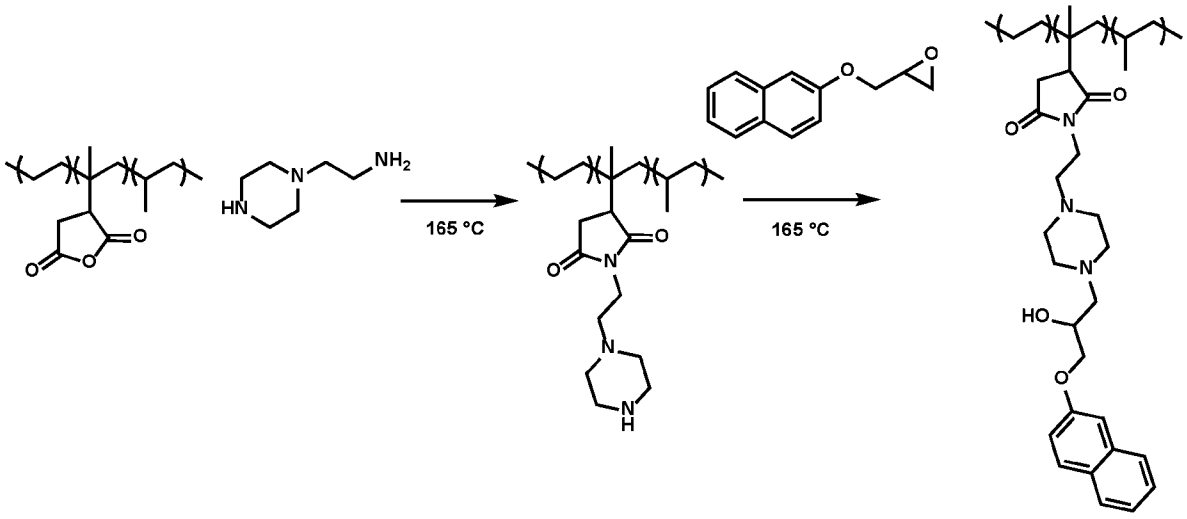
[91] In a separate vessel, Example 11 polymer was mixed with mineral oil to obtain a 55% polymer solution. This mixture (1420.5 g, 55% polymer) was slowly charged to the 4-liter reactor at 75 ± 5°C without agitation to achieve a final dilution of 40% polymer in oil. Temperature of reactor was increased to 165 ± 5°C without agitation and held for 2 hours. Next, the reaction was stirred for 1.5 hours while maintaining the temperature at 165 ± 5°C. Once hold is complete, 2-naphthyl glycidyl ether (NGE: 78.54 g) was added to the reaction mixture. The reaction was held at 165 ± 5°C for 3 hours.

Example 13 - Maleation

[92] Ethylene-propylene copolymer (3011.2 g, KV100 ~2000 cSt) was transferred into a stirred 4-liter stainless steel reactor equipped with charging lines for maleic anhydride and di-t-amyl peroxide and blanketed with nitrogen. The copolymer was heated to 170°C.

[93] Maleic anhydride (77.21 g) and di-tert-amyl peroxide (18.33 g) were charged at a constant rate simultaneously into the reactor agitation zone over a 2-hour period. After the charging, the reactor was held at temperature for an additional 15 minutes. The reaction was monitored for completeness via FT-IR. The reaction mixture was stirred at temperature for another 15 min before concluding the reaction. The maleated ethylene-propylene copolymer has an Mn 7172 based on gel permeation chromatography (calibrated by polystyrene standard).

Example 14 - Imidation and Post-Treatment



[94] The maleated ethylene-propylene copolymer from Example 13 (1008.9 g) and 100 neutral oil (1513.6 g) were charged in a stirred 4-liter glass reactor equipped with an overhead stirrer, nitrogen sweep, heating mantle, and temperature controller. Aminoethylpiperazine (AEP: 33.28 g) was added to the reactor. The reaction was held at 165°C for 2.5 hours. Upon completion of the imidation reaction, 2-naphthyl glycidyl ether (NGE: 51.59 g) was then added to the reaction mixture. Reaction was held at 165°C for 3 hours.

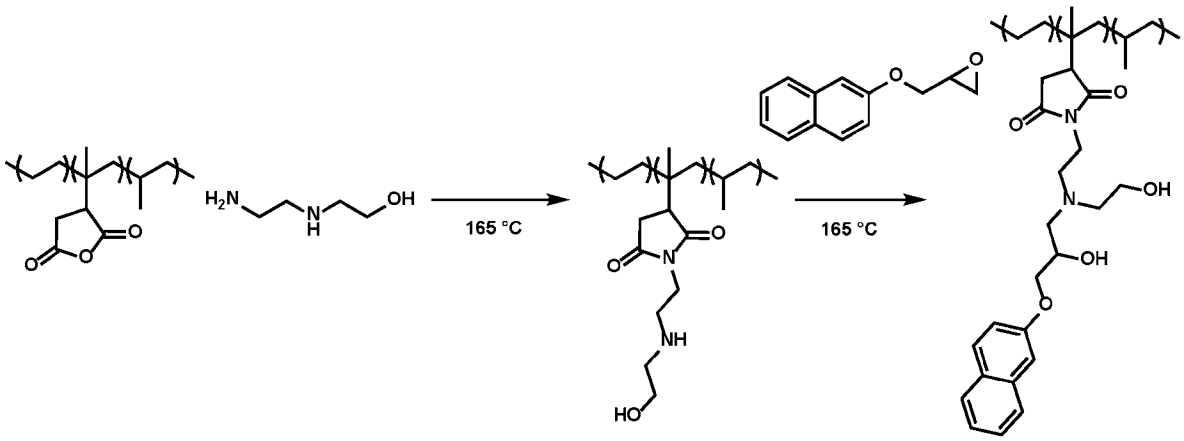
Example 15 - Maleation

[95] Ethylene-propylene copolymer (3006.5 g, KV100 ~2000 cSt) was transferred into a stirred 4-liter stainless steel reactor equipped with charging lines for maleic anhydride and di-t-amyl peroxide and blanketed with nitrogen. The copolymer was heated to 170°C.

[96] Maleic anhydride (92.98 g) and di-tert-amyl peroxide (12.19 g) were charged at a constant rate simultaneously into the reactor agitation zone over a 2-hour period. After the charging, the reactor was held at temperature for an additional 15 minutes. The reaction was monitored for completeness via FT-IR. The reaction mixture was stirred at temperature for another 15 min before

concluding the reaction. The maleated ethylene-propylene copolymer has an Mn 6433 based on gel permeation chromatography (calibrated by polystyrene standard).

Example 16 - Imidation and Post-Treatment



[97] The maleated ethylene-propylene copolymer from Example 15 (221.7 g) and 100 neutral oil (221.7 g) were charged to a stirred 1-liter glass reactor equipped with a condenser and nitrogen sweep. The mixture was heated to 165°C while being stirred. Aminoethylethanolamine (AEEA: 7.09 g) was added to the reactor. The reaction mixture was held at 165°C for 2.5 hours. Upon completion of the imidation reaction, 2-naphthyl glycidyl ether (NGE: 13.64 g) was then added to the reaction mixture. The reaction was held at 165°C for 3 hours.

Performance Testing

[98] The oil samples with 2 wt% active polymeric dispersants in Group II base oil were mixed with 3 wt% carbon black (Vulcan XC-72R) using acoustic mixer. The samples were tested in LUMiSizer® at 80°C immediately. Extinction of transmitted light was measured versus time which is related to sedimentation velocity or stability of the dispersion. Less stable dispersions form larger particles which settle more rapidly. More stable dispersions have lower sedimentation

velocities. The results summarized in the table below show that post-treatment with naphthyl glycidyl ether improves the performance:

	Polymeric dispersant functional groups (mole ratio)	Polymeric Dispersant wt%	LUMiSizer® sedimentation velocity (μm/s)
Comp. Ex. 4	AEP	2.0	2.4805
Ex. 5	AEP:NGE = 1:1	2.0	0.3176
Comp. Ex. 7	NPPDA	2.0	1.6593
Ex. 8	NPPDA:NGE = 1:1	2.0	0.2615
Comp. Ex. 9	MeDAP	2.0	0.5213
Ex. 10	MeDAP:NGE = 1:1	2.0	0.3759

Cummins® ISB Test

[99] The Cummins® ISB test is an industry standard Diesel engine durability test using a Cummins® 5.9 L ISB engine. The test lasts 350 hr and consists of two stages: a 100 hr soot generation stage followed by a 250 hr cyclic stage to induce valve train wear.

[100] Upon completion of the test cycle, the engine is dismantled and the Cam and Tappets are analyzed for wear. The Cam wear is reported in average cam scar width ACSW (μm), and the Tappet is reported as average tappet weight loss ATWL (mg). Pass/fail limits are 55 μm Cam wear and 100 mg Tappet weight loss.

	Comparative Example A	Inventive Example B
Polymeric Dispersant from Ex. 6	-	1 wt%
Avg Camshaft Wear (μm)	58.4	48.3
Avg Tappet wear (mg)	85.2	68.1

Comparative Example A

An SAE 5W-30 lubricating oil was preparing by blending the following components together with Group III base oils: succinimide dispersants; phenate detergents; sulfonate detergents; antioxidants; secondary ZnDTP; silicon-based foam inhibitor; and viscosity modifier.

Inventive Example B

Inventive Example B is the same formulation used for Comparative Example A with the addition of 1 wt% of Polymeric Dispersant from Example 6, a scaled-up synthesis as described in Example 5.

[101] The bench and engine test data shown here indicate that a liquid hydrocarbon polymer having number average molecular weight (Mn) from about 1,500 and about 16,000, functionalized with an ethylenically unsaturated acylating grafting agent, reacted with a post-treatable polyamine, then post-treated with naphthyl glycidyl ether has improved soot handling performance over the non-post-treated examples. Using data from the LUMiSizer®, samples with a sedimentation velocity similar to or better than Example 5 are considered to have good soot handling performance, i.e., Example 12, 14, and 16.

	Polymeric dispersant functional groups (mole ratio)	Polymeric Dispersant wt%	LUMiSizer® sedimentation velocity (μm/s)
Ex. 5	AEP:NGE = 1:1	2.0	0.3176
Ex. 12	AEP:NGE = 1:1	2.0	0.0811
Ex. 14	AEP:NGE = 1:1	2.0	0.2925
Ex. 16	AEEA:NGE = 1:1	1.5	0.0741

[102] It will be understood that various modifications may be made to the embodiments disclosed herein. Therefore, the above description should not be construed as limiting, but merely as

exemplifications of embodiments of the invention. For example, the functions described above and implemented for operating are for illustration purposes only. Other arrangements and methods may be implemented by those skilled in the art without departing from the scope and spirit of this application. Moreover, those skilled in the art will envision other modifications within the scope and spirit of the claims appended hereto.

CLAIMS

1. A low molecular weight polymeric dispersant composition, wherein the polymeric dispersant is represented by the following generalized structure:

$$A\text{-}[B\text{-}C\text{-}D]_n$$

wherein A is liquid hydrocarbon polymer, B is alkyl imide or alkyl amide, C is polyamine, alkyl amine, alkyl ether amine or alkyl hydroxyl amine, and D is 1-(arene-2-yloxy)propan-2-ol; and n is 1 to 15.

2. The low molecular weight polymeric dispersant composition of claim 1, wherein A is ethylene-propylene copolymer, ethylene-based polymer or propylene-based polymer.

3. The low molecular weight polymeric dispersant composition of claim 1, wherein n is 3 to 9.

4, The low molecular weight polymeric dispersant composition of claim 1, wherein the liquid hydrocarbon polymer has a number average molecular weight (Mn) from about 1,500 to about 16,000.

5. The low molecular weight polymeric dispersant composition of claim 1, wherein the low molecular weight polymeric dispersant is a reaction product of:

a liquid hydrocarbon polymer having a number average molecular weight (M_n) from about 1,500 and about 16,000;

an ethylenically unsaturated acylating grafting agent;

a polyamine having the following structure:

$$H_2N-X-Y$$

wherein X is C_2-C_{10} hydrocarbyl group, amino alkyl group, ether group, thioether group, or aromatic group and Y is amino C_1-C_{10} hydrocarbyl group, amino alkyl hydroxyl group, amino alkyl ether group, amino alkyl thioether group, amino aromatic group, or piperazine; and

aryl glycidyl ether;

or the reaction product of:

a liquid hydrocarbon polymer having a number average molecular weight (M_n) from about 1,500 and about 16,000;

an allyl or vinyl aminic grafting agent represented by the following generalized structure:

$$W-Z$$

wherein W is vinyl, alkyl vinyl, allyl, or alkyl allyl group and Z is piperazine, alkylamine, arylamine, formamide, alkyl carbamide, alkyl amide, or aryl amide; and

aryl glycidyl ether.

6. The low molecular weight polymeric dispersant composition of claim 5, wherein the aryl glycidyl ether is added as a post-treatment.

7. The low molecular weight polymeric dispersant composition of claim 5, wherein the ethylenically unsaturated acylating agent is acrylic acid, crotonic acid, methyacrylic acid, maleic

acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, chloromaleic acid, aconitic acid, methylcrotonic acid, sorbic acid or an anhydride thereof or an ester thereof.

8. The low molecular weight polymeric dispersant composition of claim 5, wherein the allyl or vinyl aminic grafting agent is 1-ethenylpiperazine, 1-(prop-1-en-2-yl)piperazine, 1-allylpiperazine, N-allylmethylamine, allylcyclohexylamine, N-allylaniline, N,2-dimethyl-2-propen-1-amine, N-ethyl-2-methylallylamine, 1-(2-methylprop-2-en-1-yl)piperazine, N-vinylformamide, N-vinylacetamide, N-vinylbenzamide, or methyl vinylcarbamate.

9. The low molecular weight polymeric dispersant composition of claim 5, wherein the polyamine is aminoethylpiperazine, N-phenyl-p-phenylenediamine, or aminoethylethanolamine.

10. The low molecular weight polymeric dispersant composition of claim 5, wherein the aryl glycidyl ether is a 2-naphthyl glycidyl ether.

11. A lubricating oil composition comprising:

a major amount of a base oil of lubricating viscosity; and

a low molecular weight polymeric dispersant represented by the following generalized structure:

$$A\text{-}[B\text{-}C\text{-}D]_n$$

wherein A is liquid hydrocarbon polymer, B is alkyl imide or alkyl amide, C is polyamine, alkyl amine, alkyl ether amine or alkyl hydroxyl amine, and D is 1-(arene-2-yloxy)propan-2-ol; and n is 1 to 15.

12. The lubricating oil composition of claim 11, wherein A is ethylene-propylene copolymer, ethylene-based polymer, or propylene-based polymer.

13. The lubricating oil composition of claim 11, wherein n is 3 to 9.

14. The lubricating oil composition of claim 11, wherein the liquid hydrocarbon polymer has a number average molecular weight (Mn) from about 1,500 to about 16,000

15. The lubricating oil composition of claim 11, wherein the polymeric dispersant is the reaction product of:

a liquid hydrocarbon polymer having a number average molecular weight (M_n) from about 1,500 and about 16,000;

an ethylenically unsaturated acylating grafting agent;

a polyamine having the following structure:

$$H_2N-X-Y$$

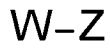
wherein X is C_2-C_{10} hydrocarbyl group, amino alkyl group, ether group, thioether group, or aromatic group and Y is amino C_1-C_{10} hydrocarbyl group, amino alkyl hydroxyl group, amino alkyl ether group, amino alkyl thioether group, amino aromatic group, or piperazine; and

aryl glycidyl ether;

or wherein the polymeric dispersant is the reaction product of:

a liquid hydrocarbon polymer having a number average molecular weight (M_n) from about 1,500 and about 16,000;

an allyl or vinyl aminic grafting agent represented by the following generalized structure:



wherein W is vinyl, alkyl vinyl, allyl, or alkyl allyl group and Z is piperazine, alkylamine, arylamine, formamide, alkyl carbamide, alkyl amide, or aryl amide; and

aryl glycidyl ether.

16. The lubricating oil composition of claim 15, wherein the polyamine is Aminoethylpiperazine, N-phenyl-p-phenylenediamine, or aminoethylethanolamine.

17. The lubricating oil composition of claim 15, wherein the allyl or vinyl aminic grafting agent is 1-ethenylpiperazine, 1-(prop-1-en-2-yl)piperazine, 1-allylpiperazine, N-allylmethylamine, allylcyclohexylamine, N-allylaniline, N,2-dimethyl-2-propen-1-amine, N-ethyl-2-methylallylamine, 1-(2-methylprop-2-en-1-yl)piperazine, N-vinylformamide, N-vinylacetamide, N-vinylbenzamide, or methyl vinylcarbamate.

18. The lubricating oil composition of claim 15, wherein the aryl glycidyl ether is a 2-naphthyl glycidyl ether.

19. A method for improving wear or soot dispersion in an internal combustion engine, the method comprising lubricating the engine with a lubricating oil composition comprising:

a major amount of a base oil of lubricating viscosity; and

a low molecular weight polymeric dispersant represented by the following generalized structure:

$$A\text{-}[B\text{-}C\text{-}D]_n$$

wherein A is liquid hydrocarbon polymer, B is alkyl imide or alkyl amide, C is polyamine, alkyl amine, alkyl ether amine or alkyl hydroxyl amine, and D is 1-(arene-2-yloxy)propan-2-ol; and n is 1 to 15.

20. The method of claim 19, wherein A is ethylene-propylene copolymer, ethylene-based polymer or propylene-based polymer.

21. The method of claim 19, wherein n is 3 to 9.

22. The method of claim 19, wherein the liquid hydrocarbon copolymer has a number average molecular weight (Mn) from about 1,500 to about 16,000

23. The method of claim 19, wherein the polymeric dispersant is the reaction product of:

a liquid hydrocarbon polymer having a number average molecular weight (M_n) from about 1,500 and about 16,000;

an ethylenically unsaturated acylating grafting agent;

a polyamine having the following structure:

$$H_2N-X-Y$$

wherein X is C_2-C_{10} hydrocarbyl group, amino alkyl group, ether group, thioether group, or aromatic group and Y is amino C_1-C_{10} hydrocarbyl group, amino alkyl hydroxyl group, amino alkyl ether group, amino alkyl thioether group, amino aromatic group, or piperazine; and

aryl glycidyl ether;

or wherein the polymeric dispersant is the reaction product of:

a liquid hydrocarbon polymer having a number average molecular weight (M_n) from about 1,500 and about 16,000;

an allyl or vinyl aminic grafting agent represented by the following generalized structure:

$$W-Z$$

wherein W is vinyl, alkyl vinyl, allyl, or alkyl allyl group and Z is piperazine, alkylamine, arylamine, formamide, alkyl carbamide, alkyl amide, or aryl amide; and

aryl glycidyl ether.

24. The method of claim 23, wherein the polyamine is an Aminoethylpiperazine, N-phenyl-p-phenylenediamine, or aminoethylethanolamine.

25. The method of claim 23, wherein the allyl or vinyl aminic grafting agent is 1-ethenylpiperazine, 1-(prop-1-en-2-yl)piperazine, 1-allylpiperazine, N-allylmethylamine, allylcyclohexylamine, N-allylaniline, N,2-dimethyl-2-propen-1-amine, N-ethyl-2-

methylallylamine, 1-(2-methylprop-2-en-1-yl)piperazine, N-vinylformamide, N-vinylacetamide, N-vinylbenzamide, or methyl vinylcarbamate.

26. The method of claim 23, wherein the aryl glycidyl ether is a 2-naphthyl glycidyl ether.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/034405

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10M149/02 C08F8/32 C08F222/06 C08F255/02 C08F255/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10M C08F C10N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2022/018681 A1 (CHEVRON ORONITE CO [US]) 27 January 2022 (2022-01-27) paragraphs [0002] - [0005]; claims; examples	1-26
A	US 2016/361699 A1 (FLOYD III WILLIAM C [US] ET AL) 15 December 2016 (2016-12-15) claims; examples	1-26

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 October 2024	17/10/2024

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/034405

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CN 116134119 A	16-05-2023
		EP 4185672 A1	31-05-2023
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