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(54) Title: FUNCTIONALIZED OLEFIN COPOLYMER

(57) Abstract: The invention relates to a novel functionalized olefin copolymer comprises an acylated polymer fully capped with a first and a second polyamine, wherein the first polyamine comprises an aromatic primary amine function, the second polyamine comprises one aliphatic primary amine function, and the molar ratio of first to second amine is greater than 3:2. The invention further relates to an oil concentrate according to the invention contains, on an active ingredient basis, 20 to 90 weight percent of a carrier or diluent oil and from about 3 to 45 weight percent of the functionalized olefin copolymer of the invention. The invention also relates to a process for preparing the functionalized olefin copolymer additive of the invention.



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FUNCTIONALIZED OLEFIN COPOLYMER

TECHNICAL FIELD

This invention relates to a novel functionalized olefin copolymer that
5 provides dispersancy properties as well as viscosity index improver credit, improved
fuel economy and good low temperature viscometric properties.

The invention further relates to a novel fuel and lubricating oil
composition containing said functionalized olefin copolymer.

The invention also relates to the process for preparing said novel
10 functionalized olefin copolymer.

BACKGROUND OF THE INVENTION

The art contains many disclosures on the use of polymer additives in
lubricating oil compositions. Ethylene α -olefin non-conjugated diene terpolymers and
15 ethylene propylene copolymers which have been further derivatized to provide
bifunctional properties in lubricating oil compositions illustrate this type of oil additive.

U.S. Pat. No. 4,089,794 discloses ethylene copolymers derived from
ethylene and one or more C_3 to C_{28} alpha olefin solution grafted with an ethylenically-
unsaturated carboxylic acid material followed by a reaction with a poly-functional
20 material reactive with carboxyl groups, such as a polyamine, a polyol, or a
hydroxylamine which reaction product is useful as a sludge and varnish control additive
in lubricating oils.

U.S. Pat. No. 4,137,185 discloses a stabilized imide graft of an
ethylene copolymer additive for lubricants.

25 U.S. Pat. No. 4,146,489 discloses a graft copolymer where the
backbone polymer is an oil-soluble ethylene-propylene copolymer or an ethylene-
propylene-diene modified terpolymer with a graft monomer of N-vinyl-pyridine or N-
vinylpyrrolidone to provide a dispersant VI improver for lubricating oils.

U.S. Pat. No. 4,320,019 discloses a multipurpose lubricating additive
30 prepared by the reaction of an interpolymer of ethylene and a C_3 - C_8 alpha-monoolefin
with an olefinic carboxylic acid acylating agent to form an acylating reaction
intermediate which is then reacted with an amine.

U.S. Pat. No. 4,340,689 discloses a process for grafting a functional
organic group onto an ethylene copolymer or an ethylene-propylene-diene terpolymer.

U.S. Pat. No. 4,357,250 discloses a reaction product of a copolymer and an olefin carboxylic acid via the "ene" reaction followed by a reaction with a monoaminepolyamine mixture.

U.S. Pat. No. 4,382,007 discloses a dispersant-VI improver prepared
5 by reacting a polyamine-derived dispersant with an oxidized ethylene-propylene polymer or an ethylene-propylene diene terpolymer.

U.S. Pat. No. 4,144,181 discloses polymer additives for fuels and lubricants comprising a grafted ethylene copolymer reacted with a polyamine, polyol or hydroxyamine and finally reacted with an alkaryl sulfonic acid.

10 WO 96/39477 teaches multi-grade lubricating oils comprising a low saturate basestock, less than three mass percent of an ashless dispersant and a viscosity modifier. The reference does not teach the multi-functional VI modifiers of the present invention.

WO 94/13763 discloses mixed ethylene alpha olefin copolymer
15 multifunctional viscosity modifiers. The reference does not teach the multi-functional VI modifiers of the present invention.

U.S. Pat. No. 4,863,623 teaches multifunctional olefin copolymer VI improvers. This patent does not teach the multi-functional VI improvers of the present invention.

20 U.S. Pat. No. 5,075,383 discloses a process for preparing a dispersant and antioxidant olefin copolymer additives, wherein free radical grafting is accompanied by the molecular weight reduction of the copolymers due to mechanically shearing.

U.S. Pat. No. 5,556,923 discloses oil solutions of adducted
25 derivatized EPR or EPDM. This patent does not teach the multi-functional VI improvers of the present invention.

U.S. Pat. No. 5,780,540 discloses the process of functionalizing a hydrogenated diene copolymer consecutively with 2 amines adding antioxidant properties to the functionalized hydrogenated diene copolymer. This patent does not
30 teach the process of the present invention.

U.S. Pat. No. 5,942,471 discloses a functionalized olefin copolymer prepared by attaching two antioxidants to the polymeric chain. The claimed benefit is an improved oxidation stability resulting in a lower viscosity increase in an engine test. The patent does not teach the amine combination and advantages of the multi-
35 functional VI improvers of the present invention.

U.S. Pat. No. 6,107,258 discloses a functionalized olefin copolymer comprising the reaction product of a) an acylated olefin copolymer, wherein said acylated olefin copolymer comprises an olefin copolymer substrate grafted with from about 0.5 to about 6 molecules of ethylenically unsaturated carboxylic acid, per
5 molecule of olefin copolymer; b) at least one coupling compound, wherein said coupling compound contains more than one amine functionality capable of reacting with the acylated olefin copolymer and c) an aromatic amine performance enhancing compound and wherein the acylated olefin copolymer is reacted with from 0.5 to 85 mol% coupling compound and 15 to 99.5 mol% performance enhancing compound per
10 mol of acylating agent. The polyamine coupling compounds disclosed in U.S. Pat. No. 6,107,258 are diamines or triamines with at least two primary amines.

A problem of the known additives is that the viscosity of a lubricating oil compositions containing said additive increases during transport and storage.

Secondly, remaining aromatic primary amines are sensitive for
15 oxidation, thus rapidly causing lubricant oil to discolorate. This requires that low molecular weight alcohols and aldehydes have to be added to oil comprising the imidized polymer according to the state of the art to cap the acyl and primary amine groups.

An object of this invention is to provide a novel functionalized olefin
20 copolymer, which, when used in a fuel or lubricant composition, results in a enhanced stability of the viscosity of said composition.

Another object of the present invention is to provide a process, for preparing an imidized polymer with an as low as possible amount of free and amid-bound polyamine.

25 A further object of the invention is to provide a highly grafted, multi-functional lubricant additive effective for improving viscosity index, dispersancy and antioxidant properties of a lubricating oil composition, as well as enabling extended lubricant drain intervals and improving fuel economy and fuel economy durability.

A further object is to provide a novel lubricating oil concentrate
30 containing the highly grafted, multi-functional olefin copolymer additive of the invention as well as to provide concentrates of the novel functionalized olefin copolymer of invention.

A further object is to provide a method for manufacturing a novel functionalized olefin copolymer for use as lubricant additive.

SUMMARY OF THE INVENTION

The novel functionalized olefin copolymer comprises a reaction product of an acylated ethylene α -olefin copolymer and a first and a second polyamine, wherein the first polyamine comprises an aromatic primary amine function, the second
5 polyamine comprises one aliphatic primary amine function, and the molar ratio of first to second amine is greater than 3:2, preferably greater than 3:1, with more preference greater than 4:1.

An oil concentrate according to the invention contains, on an active ingredient basis, 20 to 90 weight percent of a carrier or diluent oil and from about 3 to
10 45 weight percent of the functionalized olefin copolymer of the invention.

Process for preparing a functionalized olefin copolymer according to the invention comprises contacting an acylated olefin copolymer with a first polyamine comprising an aromatic primary amine function, until a partially capped olefin copolymer is formed and wherein the partially capped olefin copolymer is subsequently
15 contacted with a second polyamine comprising an aliphatic primary amine function such that a fully capped olefin copolymer is formed, wherein the molar ratio of first to second amine is greater than 3:2, preferably greater than 3:1, with more preference greater than 4:1.

20

DETAILED DESCRIPTION OF THE INVENTION

The novel functionalized olefin copolymer comprises a reaction product of an acylated ethylene α -olefin copolymer which can be obtained by reacting an ethylenically unsaturated carboxylic acid material with an ethylene α -olefin
25 copolymer.

The ethylene α -olefin copolymers employed in forming the novel functionalized olefin copolymer of the present invention are copolymers of ethylene and one or more C_3 to C_{23} α -olefins. Copolymers of ethylene and propylene are most preferred. Other α -olefins suitable to form the copolymer or to be used in combination
30 with ethylene and propylene to form a terpolymer include 1-butene, 1-pentene, 1-hexene, 1-octene, and styrene; also α,ω -diolefins such as 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, etc., also branched chain alpha-olefins such as 4-methylbutene-1, 5-methylpentene-1 and 6-methylheptene-1 and mixtures thereof.

The ethylene α -olefin copolymers may contain minor amounts of other olefinic monomers such as conjugated or nonconjugated dienes, and/or ethylenically unsaturated carboxylic compounds, so long as the basic characteristics (e.g. crystallinity and solubility in natural or synthetic oils) of the ethylene α -olefin copolymers are not materially changed.

The polymerization reaction used to form the ethylene α -olefin copolymer substrate is generally carried out in the presence of a conventional Ziegler-Natta or metallocene catalyst system. The polymerization medium is not specific and can include solution, slurry, or gas phase processes, as known to those skilled in the art. When solution polymerization is employed, the solvent may be any suitable inert hydrocarbon solvent that is liquid under reaction conditions for polymerization of α -olefins; examples of satisfactory hydrocarbon solvents include straight chain paraffins having from 5 to 8 carbon atoms, with hexane being preferred. Aromatic hydrocarbons, preferably aromatic hydrocarbon having a single benzene nucleus, such as benzene, toluene and the like; and saturated cyclic hydrocarbons having boiling point ranges approximating those of the straight chain paraffinic hydrocarbons and aromatic hydrocarbons described above, are particularly suitable. The solvent selected may be a mixture of one or more of the foregoing hydrocarbons. When slurry polymerization is employed, the liquid phase for polymerization is preferably liquid propylene. It is desirable that the polymerization medium be free of substances that will interfere with the catalyst components.

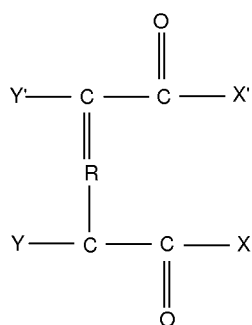
Ethylene-propylene or higher α -olefin copolymers may consist of from about 20 to 90 weight percent ethylene and from about 80 to 10 weight percent propylene or higher α -olefin with the preferred ratios being from about 30 to 75 weight percent ethylene and from about 70 to 25 weight percent of a C_3 to C_{23} α -olefin. The most preferred copolymers for practice of this invention are comprised of from 45 to 70 weight percent ethylene and 55 to 30 weight percent propylene.

The number average molecular weight as determined by gel permeation chromatography, M_n , of the copolymer substrate employed in the present invention is between 700 and 500,000, preferably between about 3,000 and about 100,000, more preferably between about 10,000 and about 50,000. The molecular weight distribution, M_w/M_n , of the polymer substrates of the present invention is less than 15, preferably from 1.0 to 10.

The term copolymer is used generically to encompass copolymers or terpolymers.

An ethylenically unsaturated carboxylic acid material is grafted onto the prescribed polymer backbone to form an acylated ethylene α -olefin copolymer.

- 5 These carboxylic reactants which are suitable for grafting onto the ethylene α -olefin copolymer contain at least one ethylenic bond and at least one, preferably two, carboxylic acid or its anhydride groups, or derivatives thereof. Preferably, the carboxylic reactants are selected from the group consisting of acrylic, methacrylic, cinnamic, crotonic, and maleic, fumaric, and itaconic reactants of the general formula:



10

- wherein R is an alkyl group having from 0-4 carbon atoms, X and X' are the same or different and are independently selected from the group consisting of -OH, -O-hydrocarbyl, -O-M⁺ wherein M⁺ represents one equivalent of metal, ammonium or amine cation, -NH₂, -Cl, -Br, and together X and X' can be -O- so as to form the anhydride, and Y and Y' are the same or different and are independently selected from the group consisting of hydrogen, branched or straight chain alkyls having 1-12 carbon atoms, a halogen atom, or an organo anhydride, ketone, or heterocyclic group having 2-12 carbon atoms. Ordinarily, the maleic or fumaric reactants will be maleic acid, fumaric acid, maleic anhydride, or a mixture of two or more of these. Maleic anhydride is generally preferred due to its commercial availability and ease of reaction.

- The carboxylic reactant is grafted onto the prescribed polymer backbone in an amount of from about 0.5 to about 5 wt% of carboxylic reactant per 100% of the polymer backbone, preferably, at least 1 wt% of the carboxylic reactant per 100% of polymer backbone. More preferably, at least 2 wt%. of the carboxylic reactant are reacted with 100 wt% of the polymer backbone. Throughout the specification this is referred to as the carboxylic reactant/olefin copolymer ratio.

- The grafting reaction to form the acylated olefin copolymers is generally carried out with the aid of a free-radical initiator either in solution or in bulk, as in an extruder or intensive mixing device. When the polymerization is carried out in

hexane solution, it is economically convenient to carry out the grafting reaction in hexane as described in U.S. Pat. Nos. 4,340,689, 4,670,515 and 4,948,842. The resulting polymer intermediate is characterized by having carboxylic acid acylating functionality randomly within its structure.

5 In the bulk process for forming the acylated ethylene α -olefin copolymers, the ethylene α -olefin copolymer is fed to rubber or plastic processing equipment such as an extruder, intensive mixer or masticator, heated to a temperature of 150 to 400 °C and the ethylenically unsaturated carboxylic acid reagent and free-radical initiator are separately co-fed to the molten polymer to effect grafting. The
10 reaction is carried out optionally with mixing conditions to effect shearing and grafting of the ethylene α -olefin copolymers according to U.S. Pat. No. 5,075,383. The processing equipment is generally purged with nitrogen to prevent oxidation of the polymer and to aid in venting unreacted reagents and byproducts of the grafting reaction. The residence time in the processing equipment is sufficient to provide for the
15 desired degree of acylation and to allow for purification of the acylated ethylene α -olefin copolymer via venting. Mineral or synthetic lubricating oil may optionally be added to the processing equipment after the venting stage to dissolve the acylated copolymer.

 The free-radical initiators which may be used to graft the ethylenically unsaturated carboxylic acid material to the polymer backbone include peroxides,
20 hydroperoxides, peresters, and also azo compounds and decompose thermally within the grafting temperature range to provide free radicals. Representatives of these free-radical initiators are azobutyronitrile, dicumyl peroxide, 2,5-dimethylhexane-2,5-bis-tertiarybutyl peroxide and 2,5-dimethyl-hex-3-yne-2,5-bis-tertiary-butyl peroxide, bis-tertiary-butyl peroxide, 3,3,5,7,7-pentamethyl 1,2,4-trioxepane and 3,6,9-triethyl-3,6,9-
25 trimethyl-1,4,7-triperoxonane. The initiator is used in an amount of between about 0.005% and about 1% by weight based on the weight of the reaction mixture.

 Other methods known in the art for effecting reaction of ethylene α -olefin copolymers with ethylenic unsaturated carboxylic reagents such as halogenation reactions, thermal or "ene" reactions or mixtures thereof can be used instead of the
30 free-radical grafting process. Such reactions are conveniently carried out in mineral oil or bulk by heating the reactants at temperatures of 250 to 400 °C. under an inert atmosphere to avoid the generation of free radicals and oxidation byproducts.

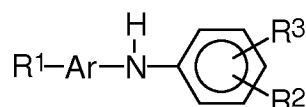
 The acylated ethylene α -olefin copolymers are reacted with a first polyamine, in order to produce a functionalized olefin copolymer which exhibits, for

example, additional dispersancy properties, improved antioxidancy, and/or antiwear properties.

The first polyamine comprises an aromatic primary amine, capable of reaction with the carboxylic group of the acylated ethylene α -olefin copolymer and another functional group, such as a heterocyclic or conjugated aromatic unit, or a combination thereof, to provide additional performance criteria. The term "additional performance criteria" refers to desired chemical and physical properties or functions which the functionalized olefin copolymer imparts as additives to lubricating oil or fuel in addition to basic viscosity index/dispersancy improvements.

Preferred examples of aromatic primary amine comprising polyamines are N-phenyl-phenylene diamine (NPPDA), N-naphthyl-phenylene diamine, and

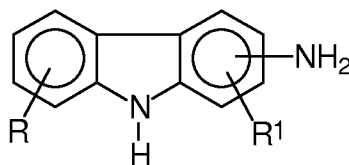
(a) substituted forms thereof as represented by the formula:



in which Ar is aromatic and R^1 is $-H$, $-(NH-Aryl)_n-H$, $-(NH-Alkyl)_n-H$, $-NH-arylalkyl$, a branched or straight chain radical having from 4 to 24 carbon atoms that can be alkyl, alkenyl, alkoxy, aralkyl, alkaryl, hydroxyalkyl or aminoalkyl, R^2 is $(-NH_2, -aryl-NH_2)$, in which n has a value from 1 to 10, and R^3 is hydrogen, alkyl, alkenyl, alkoxy, aralkyl, alkaryl having from 4 to 24 carbon atoms,

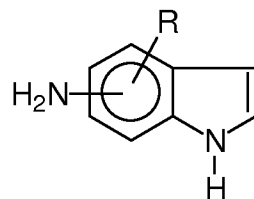
Preferred heterocyclic polyamines are selected from the groups represented by the formula:

(b) an aminocarbazole



in which R and R' represent hydrogen, or an alkyl, alkenyl, or alkoxy radical having 1 to 14 carbon atoms;

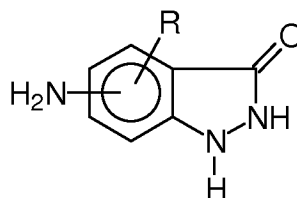
(c) an aminoindole represented by the formula:



in which R represents hydrogen or an alkyl radical having from 1 to 14 carbon atoms,

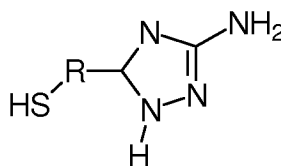
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(d) an amino-indazolinone represented by the formula:



in which R is hydrogen or an alkyl radical having from 1 to 14 carbon atoms,

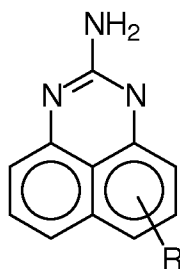
(e) an aminomercaptotriazole represented by the formula:



10

in which R can be absent or can be C₁ – C₁₀ linear or branched hydrocarbon selected from the group consisting of alkyl, aryl, alkaryl, or arylalkyl.

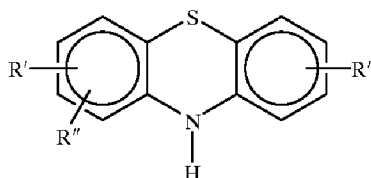
(f) an aminopyrimidine represented by the formula:



15

in which R represents hydrogen or an alkyl or alkoxy radical having from 1 to 14 carbon atoms.

(g) an aminophenothiazine



in which R' is NH₂-, NH₂-aryl-, NH₂-arylalkyl-, R'' is H or a (C₁-C₂₄) branched or straight chain alkyl, alkenyl, alkoxy or arylalkyl.

Preferably, the first polyamine is NPPDA.

5 The first polyamine is present in variable amounts depending upon the desired properties of the final product. Preferably, the first polyamine will be present in an amount of from 60 to 98 mol% per mol of acylating agent.

Use of preferred performance enhancing compounds is described in U.S. Pat. No.

4,863,623, 5,075,383, 5,112,508, 5,147,569, 5,160,446, 5,162,086, 5,167,845,
10 5,188,745, 5,200,100, 5,200,102, 5,238,588, 5,275,746, 5,409,623, 5,424,366,
5,429,757, 5,472,627, 5,474,694, 5,534,171, and 5,563,118.

If the first polyamine is present at a level below 60 mol%, the concerned final product will substantially lack the required performance characteristics of a functionalized olefin copolymer according to the invention. Further, as will be
15 demonstrated later, a level of more than 98 mol% of the first polyamine in the final product requires substantially increased reaction times and/or temperatures.

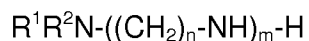
The functionalized olefin copolymer further comprises a second polyamine that comprises only one aliphatic primary amine function.

Suitable second polyamines include aliphatic, cycloaliphatic, and
20 heterocyclic amines, capable of reacting with the carboxylic functionality of the acylated olefin copolymer and characterized by the general formula:



in which n and m are intergers independently selected from 2-10,

R¹ is hydrogen, -aryl, naphthyl, -alkylaryl, -arylalkyl, -aryl-NH-aryl, a branched or
25 straight chain radical having from 1 to 24 carbon atoms selected from the group of alkyl, alkenyl, alkoxyl, hydroxyalkyl, or aminoalkyl or



in which n and m are independently selected from 1-10,

R¹ as described above and

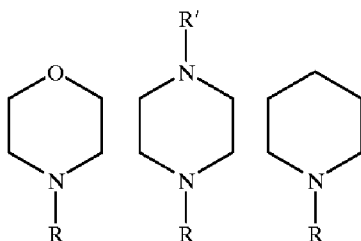
30 R² is -aryl, -naphthyl, -alkylaryl, -arylalkyl, -aryl-NH-aryl, a branched or straight chain radical having from 1 to 24 carbon atoms selected from the group of alkyl, alkenyl,

alkoxyl, hydroxyalkyl, or aminoalkyl,

wherein R^1 and R^2 are optionally linked to form a heterocycle optionally comprising a further heteroatom selected from the group consisting of O, S and N.

Such heterocycle optionally comprising O and N are

- 5 aminomorpholine, aminopiperazine, and aminopiperidine can be represented by the formula:



in which R is $-(CH_2)_n-NH)_m-H$ wherein n is a value of 1 to 10 and R' is H, alkyl, alkenyl, alkoxy, arylalkyl or alkylaryl having 1 to 24 carbon atoms.

- 10 Suitable second polyamines are N-phenylethylenediamine (PEDA), N-phenyl-ortho-phenylenediamine (OP), N-aminoethyl-N'-phenylphenylenediamine, N-aminoethylmorpholine (AEM), N-aminoethyltallowamine, N-aminoethylcocoamine, N-aminopropylmorpholine, N-aminopropyltallowamine, N-aminopropylcocoamine, dimethylaminopropylenediamine (DMPA) and 1-(2-aminoethyl)-piperazine.

- 15 Preferably the second polyamine is PEDA or AEM.

According to an embodiment of the present invention, the first and second amine are present in the functionalized copolymer at a molar ratio of at least 3:2, preferably greater than 3:1, with more preference greater than 4:1.

- 20 In consequence, the second polyamine is present in variable amounts depending upon the requirement of a fully capped olefin copolymer. Preferably, the second polyamine will be present in an amount of from 2 to 40 mol % per mol of acylating agent.

- 25 The functionalized olefin copolymer products of the present invention find their primary utility in lubricating oil compositions which employ a base oil in which the additives are dissolved or dispersed. Such base oils may be natural, synthetic or mixtures thereof. Base oils suitable for use in preparing the lubricating oil compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Advantageous results are also achieved by employing the additive mixtures of the
- 30 present invention in base oils conventionally employed in and/or adapted for use as

power transmitting fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other lubricating oil compositions can also benefit from the incorporation therein of the additive mixtures of the present invention.

5 These lubricating oil formulations conventionally contain additional additives that will supply the characteristics that are required in the formulations. Among these types of additives are included viscosity index improvers, antioxidants, corrosion inhibitors, detergents, dispersants, pour point depressants, antiwear agents, antifoamants, demulsifiers and friction modifiers.

10 In the process for preparing a functionalized olefin copolymer, an acylated ethylene α -olefin copolymer is contacted with a first polyamine, until a partially capped ethylene α -olefin copolymer is formed.

 The term "partially capped ethylene α -olefin copolymer" is used for an acylated ethylene α -olefin copolymer of which at least a part of the acyl groups have
15 been reacted with the first polyamine. The first polyamine typically has a first reactive amine group and a second less reactive amine group, such that the second amine group does not react with free acyl groups. This avoids coupling of copolymer molecules as described in U.S. Pat. No. 6,107,258.

 The advantage of preparing a partially capped ethylene α -olefin
20 copolymer is that full conversion of the first polyamine can be achieved at milder reaction conditions or after a shorter reaction time compared to an acylated ethylene α -olefin copolymer fully capped with the first polyamine as will be demonstrated by the examples. An advantage of the full conversion is the increased discoloration stability of the functionalized olefin copolymer and the related oil concentrates. Further the
25 absence of unreacted first polyamine represents a general quality improvement of the functionalized olefin copolymer and the related oil concentrates.

 After a partially capped ethylene α -olefin copolymer is formed, this partially capped ethylene α -olefin copolymer is subsequently contacted with a second polyamine comprising one aliphatic primary amine group, such that a fully capped
30 ethylene α -olefin copolymer is formed. Imidization reactivity of such aliphatic primary polyamines is substantially higher, such that an equimolar full conversion can be achieved at milder reaction conditions or after shorter reaction time compared to a reaction with only the first polyamine.

An embodiment of the process of the present invention is the separate dosing and reaction of the first and second polyamine. Dosing and reacting the 2 polyamines in the inverse order or simultaneously will negatively affect the extend of the capping reaction. No fully capped ethylene α -olefin copolymer will be obtained.

5 The term "fully capped" ethylene α -olefin copolymer is used for an acylated ethylene α -olefin copolymer of which at least 99 % of the acyl groups have been reacted with the first and the second polyamine.

10 Functionalized olefin copolymer, which, when used in a fuel or lubricant composition, result in an enhanced stability of the viscosity of said composition.

 A further advantage of the invention is that no significant surplus of amine is required to avoid free acyl groups in the functionalized ethylene α -olefin copolymer and that a fully capped ethylene α -olefin copolymer can be obtained within a short reaction time. The resulting functionalized ethylene α -olefin copolymer
15 composition is realized with a minimum level of both the first and second polyamine. The so generated composition being free of unreacted acyl groups shows lower solution viscosities as well as superior solution viscosity stability upon storage while not showing detrimental effects of excessive polyamine addition. Such detrimental effects of excess polyamine in the composition are amongst others a significant discoloration
20 of the composition or a substantially increase seal incompatibility of the composition.

 Typically, an acylated ethylene α -olefin copolymer comprising 0.5-5.0 wt % of acyl groups is mixed with 0.8-1.1 mol equivalent, with respect to the molar amount of grafted acyl groups of the first polyamine in a mineral or synthetic lubricating oil, solvent solution or polymer melt. This mixture is heated with agitation at a
25 temperature in the range of 120 to 300 °C until a capped ethylene α -olefin copolymer is formed, wherein the fraction x of the acyl groups is capped with the first polyamine. The amount (x) of capped acyl groups can easily be determined by infrared spectroscopy and is generally between 0.60 and 0.98. Subsequently, the partially capped ethylene α -olefin copolymer is contacted with $(1 - x)$ mol equivalent of the second polyamine such
30 that the acylated ethylene α -olefin copolymer is fully capped.

 These reactions are carried out conveniently in a stirred reactor under nitrogen purge. However, as obvious to one skilled in the art, equally convenient is to add the acylated ethylene α -olefin copolymer and the first, respectively second amine

to zones downstream from the graft reaction-vent zones in a twin screw extruder reactor.

The functionalized olefin copolymers of the present invention can be incorporated into a lubricating oil or a fuel in any convenient way. Thus, the functionalized olefin copolymers can be added directly to the lubricating oil or fuel by dispersing or dissolving the same in the lubricating oil or fuel at the desired level of concentration. Such blending into the lubricating oil or fuel can occur at room temperature or elevated temperatures. Alternatively, the functionalized olefin copolymers can be blended with a suitable oil-soluble solvent/diluent (such as benzene, xylene, toluene, lubricating base oils and petroleum distillates, including the various normally liquid fuels described in detail below) to form a concentrate, and then blending the concentrate with a lubricating oil or fuel to obtain the final formulation. Such additive concentrates will typically contain on an active ingredient basis from about 3 to about 45 wt. %, and preferably from about 10 to about 35 wt. %, functionalized olefin copolymer additive, and typically from about 5 to 90 wt %, preferably from about 10 to 40 wt %, base oil based on the concentrate weight.

The functionalized olefin copolymer products of the present invention possess very good dispersant properties. Accordingly, the functionalized olefin copolymer products are used by incorporation and dissolution into an oleaginous materials such as fuels and lubricating oils. When the products of this invention are used in normally liquid petroleum fuels such as middle distillates boiling from about 65 to 430 °C, including kerosene, diesel fuels, home heating fuel oil, jet fuels, etc., a concentration of the additives in the fuel in the range of typically from about 0.001 to about 0.5, and preferably 0.005 to about 0.15 weight percent, based on the total weight of the composition, will usually be employed.

The fuel compositions of this invention can contain, in addition to the products of this invention, other additives that are well known to those of skill in the art. These can include anti-knock agents, deposit preventers or modifiers, dyes, cetane improvers, antioxidants, rust inhibitors, gum inhibitors, metal deactivators, and the like.

In the preparation of lubricating oil formulations it is common practice to introduce the additives in the form of 10 to 80 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent. Usually these concentrates may be diluted with 3 to 100, e.g., 5 to 40, parts by weight of lubricating oil per part by weight of the additive package in forming finished lubricants, e.g. crankcase motor oils. The purpose of concentrates, of course, is to make the handling

of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend. Thus, the functionalized olefin copolymer would usually be employed in the form of a 10 to 50 wt. % concentrate, for example, in a lubricating oil fraction.

5 The functionalized olefin copolymers of the present invention will generally be used in admixture with a lube oil basestock, comprising an oil of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof.

10 Natural oils include animal oils and vegetable oils (e.g., castor, lard oil), liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils. The synthetic lubricating oils used in this invention include one of any number of commonly used synthetic hydrocarbon oils, which include, but are not limited to, poly-alpha-
15 olefins, alkylated aromatics, alkylene oxide polymers, interpolymers, copolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification etc, esters of dicarboxylic acids and silicon-based oils.

20 The functionalized olefin copolymers of the present invention may be post-treated so as to impart additional properties necessary or desired for a specific fuel or lubricant application. Post-treatment techniques are well known in the art and include boronation, phosphorylation, and maleination.

EXAMPLES

25 The following examples are intended to assist in further understanding of the invention. The particular materials and conditions employed are intended to be further illustrative of the invention and are not limiting upon the reasonable scope thereof.

Comparative Experiments A to H:

30 Capping with a first amine or a single amine:

 A 13.5 % oil solutions of a maleic anhydride grafted EPM were prepared. The polymeric backbone has an ethylene content of 49%, a propylene content of 51% with 2.0 wt.% of grafted maleic anhydride functional groups.

35 The capping reactions were carried out on lab scale in thick walled glass reactors in oil baths at 165°C (reaction temperature $\pm$ 160°C). Mixing of the

viscous reaction mixture was achieved by using a metal helical top stirrer. Samples were taken over time to monitor the decay of residual amine. Analysis of the products was done by GC injection of the samples dissolved in THF containing diphenylether (DPE) as an internal standard. Reactions were carried out for 6 and 24 hours reported in Table 1 and 2 respectively.

Table 1

6 hours	mol equivalent NPPDA	NPPDA imid %	unreacted NPPDA [%]
Comp. Exp. A	0.4	39.7	0.68
Comp. Exp. B	0.63	62.6	0.68
Comp. Exp. C	0.8	79.4	0.74
Comp. Exp. D	0.9	88.6	1.61
Comp. Exp. E	1	94.7	5.34

Table 2

24 hours	mol equivalent NPPDA	NPPDA imid %	unreacted NPPDA [%]
Comp. Exp. F	0.8	79.7	0.4
Comp. Exp. G	0.9	89.4	0.63
Comp. Exp., H	1	96.9	3.1

From the results of the capping with a first amine it can be observed that a drastic increase of unreacted NPPDA takes place at molar capping ratio close to equimolar conditions (Comp. Examples D, E and H); substantial amounts of NPPDA do not react. From the data shown above an optimal capping ratio for short reaction times (6 h) is represented by 0.80. If the reaction time is extended to 24 h molar capping ratios of 0.90 yield low concentrations of residual NPPDA.

Examples 1 and 2

Capping with a second amine:

The polymer solutions of the Comparative Experiments C and G (any other Comparative Experiments B to H also suffices the scope of the present application) have been subjected to a capping reaction with a second amine. The reactions were continued in the same equipment and conditions as for the comparative experiments while the judicious amount of second capping amine was dosed and the process of the reaction further followed by GC analysis. As second capping amine

AEM and PEDA were added at a level of 0.20 and 0.11 mol equivalents in examples 1 and 2 respectively. See Table 3.

Table 3

	second amine	mol equivalent Second amine	unreacted NPPDA* / Second amine** [%]		
			after 1 min	after 30 min	after 60 min
Example 1	AEM	0.20	0.76 / 10.2	0.74 / 2.1	0.78 / 0.8
Example 2	PEDA	0.11	0.65 / 14	0.73 / 5	0.71 / 2

5 * Indicated levels are a percentage of the initially dosed quantities

** Rounded values due to absolute levels being close to detection limits

In both cases a fast decay in residual second amine was observed indicating an imidization speed substantially faster and more complete than shown in
10 example 1, where an equimolar amount of NPPDA has been used.

Viscosity creep:

Viscosity creep of the prepared samples was evaluated on the samples as prepared in Atlas 100 SN (13.5% solids). For this purpose, individual lots of
15 samples were stored at and 70 °C for 1 day, 1 week and six weeks respectively. The kinematic viscosity (@100 °C) was determined by standard Ubbelohde technique.

Viscosity of the samples was monitored over time (Table 4) indicating good viscosity stability of the examples 1 and 2 over the storage period of 6 weeks.

20 Table 4

	Imid %	Unreact. amines total %	Viscosity of oil solutions [cSt]			
			Initial sample	1 day	1 week	6 weeks
Comp. Exp. H	96.9	3.1	1400	1410	1460	1600
Example 1	99.4	0.788	800	815	808	812
Example 2	99.7	0.855	850	853	846	858

As shows the evaluation of Comparative Experiment H in Table 4, the initial kinematic viscosity of the sample is substantially higher, representing a disadvantage when choosing polymer concentration for adequate handling. Further,
25 the viscosity stability of these samples is poor, which represents a further disadvantage when shipping and storing. Last but not least, the total amount of unreacted amine is

substantially higher, representing a further disadvantage of the product of Comparative Experiment H.

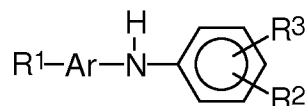
CLAIMS

1. Functionalized olefin copolymer comprising a reaction product of an acylated ethylene α -olefin copolymer and a first and a second polyamine, characterized in that
the first polyamine comprises an aromatic primary amine function,
the second polyamine comprises one aliphatic primary amine function, and
the molar ratio of first to second amine is greater than 3:2.
2. Functionalized olefin copolymer according to claim 1, wherein the second polyamine is selected from
i) an aliphatic polyamine represented by the formula :

$$R^1-((CH_2)_n-NH)_m-H$$
in which n and m are intergers independently selected from 2-10,
R¹ is hydrogen, -aryl, naphthyl, -alkylaryl, -arylalkyl, -aryl-NH-aryl, a branched or straight chain radical having from 1 to 24 carbon atoms selected from the group of alkyl, alkenyl, alkoxyl, hydroxyalkyl, or aminoalkyl and
ii) an aliphatic polyamine represented by the formula :

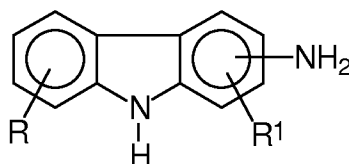
$$R^1R^2N-((CH_2)_n-NH)_m-H$$
in which n and m are independently selected from 1-10,
R¹ as described above and
R² is -aryl, -naphthyl, -alkylaryl, -arylalkyl, -aryl-NH-aryl, a branched or straight chain radical having from 1 to 24 carbon atoms selected from the group of alkyl, alkenyl, alkoxyl, hydroxyalkyl, or aminoalkyl,
wherein R¹ and R² are optionally linked to form a heterocycle optionally comprising a further heteroatom selected from the group consisting of O, S and N.
3. Functionalized olefin copolymer according to claim 1 and 2, wherein the second polyamine is selected from the group consisting of N-phenylethylenediamine (PEDA), N-aminoethyl-N'-phenylphenylenediamine, N-aminoethylmorpholine (AEM), N-aminoethyltallowamine, N-aminoethylcocoamine, N-aminopropylmorpholine, N-aminopropyltallowamine, N-aminopropylcocoamine, dimethylaminopropylenediamine (DMAPA) and 1-(2-aminoethyl)-piperazine.
4. Functionalized olefin copolymer according to claim 1 to 3, wherein the first polyamine is selected from:

(a) an N-arylphenylenediamine represented by the formula:



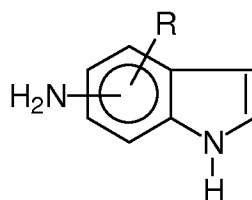
in which Ar is aromatic and R¹ is -H, -(NH-Aryl)_n-H, -(NH-Alkyl)_n-H, -NH-arylalkyl, a branched or straight chain radical having from 4 to 24 carbon atoms that can be alkyl, alkenyl, alkoxy, aralkyl, alkaryl, hydroxyalkyl or aminoalkyl, R² is (-NH₂, -aryl-NH₂, in which n has a value from 1 to 10, and R³ is hydrogen, alkyl, alkenyl, alkoxy, aralkyl, alkaryl having from 4 to 24 carbon atoms,

(b) an aminocarbazole represented by the formula:



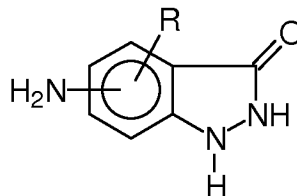
in which R and R¹ represent hydrogen or an alkyl, alkenyl, or alkoxy radical having from 1 to 14 carbon atoms,

(c) an aminoindole represented by the formula:



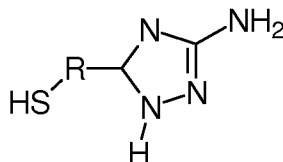
in which R represents hydrogen or an alkyl radical having from 1 to 14 carbon atoms,

(d) an amino-indazolinone represented by the formula:



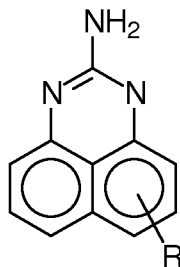
in which R is hydrogen or an alkyl radical having from 1 to 14 carbon atoms,

(e) an aminomercaptotriazole represented by the formula:



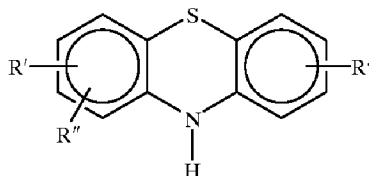
in which R can be absent or can be C₁ – C₁₀ linear or branched hydrocarbon selected from the group consisting of alkyl, aryl, alkaryl, or arylalkyl.

(f) an aminopyrimidine represented by the formula:



in which R represents hydrogen or an alkyl or alkoxy radical having from 1 to 14 carbon atoms.

(g) an aminophenothiazine



in which R' is NH₂-, NH₂-aryl-, NH₂-arylalkyl-, R'' is H or a (C₁-C₂₄) branched or straight chain alkyl, alkenyl, alkoxy or arylalkyl.

5. Functionalized olefin copolymer of claim 1 to 4, wherein the first polyamine is NPPDA.

6. An oil concentrate containing, on an active ingredient basis, 20 to 90 weight percent of a carrier or diluent oil and from about 3 to 45 weight percent of the functionalized olefin copolymer of claim 1.

7. Process for preparing a functionalized olefin copolymer according to claim 1 comprising

a. contacting an acylated ethylene α -olefin copolymer with a first polyamine comprising an aromatic primary amine function, until a partially capped olefin copolymer is formed characterized in that

- b. the partially capped ethylene α -olefin copolymer is subsequently contacted with a second polyamine comprising an aliphatic primary amine function such that a fully capped ethylene α -olefin copolymer is formed, wherein the molar ratio of first to second amine is greater than 3:2.
- 5 8. Process according to claim 7, wherein the acylated ethylene α -olefin copolymer, comprising 0.5 - 5.0 wt % of acyl groups,
- a. is contacted with 0.8-1.1 mol equivalent, with respect to the molar amount of grafted acyl groups, of the first polyamine, resulting in a capped ethylene α -olefin copolymer, wherein the fraction x of the acyl groups is capped with
- 10 the first polyamine and subsequently,
- b. contacting the partially capped ethylene α -olefin copolymer with $(1 - x)$ mol equivalent of the second polyamine and wherein x is between 0.6 and 0.98 such that the acylated ethylene α -olefin copolymer is fully capped.
9. Process according to claim 7 and 8, wherein the method is carried out in an
- 15 extruder, substantially free of solvents.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/052015

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F8/32 C10M149/06 C10M149/10
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)
C08F C10M

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 083 024 A1 (AFTON CHEMICAL CORP [US]) 29 July 2009 (2009-07-29)	1-9
Y	paragraph [0010] - paragraph [0012] paragraph [0024] - paragraph [0027] paragraph [0053] - paragraph [0059] -----	1-9
X	EP 1 916 293 A1 (CHEVRON ORONITE CO [US]) 30 April 2008 (2008-04-30) paragraph [0086] - paragraph [0119]; examples A, 2, 6 paragraph [0147] - paragraph [0148] -----	1-9
Y	US 5 075 383 A (MIGDAL CYRIL A [US] ET AL) 24 December 1991 (1991-12-24) cited in the application column 2, line 37 - column 3, line 56 column 13, line 32 - line 47 ----- -/--	1-9



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

"E" earlier document but published on or after the international filing date

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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

24 February 2011

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/052015

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96/39447 A1 (KURARAY CO [JP]; FUJIWARA NAOKI [JP]; KUSUDOU TAKESHI [JP]; KAWAHARA T) 12 December 1996 (1996-12-12) page 12, line 11 - page 13, line 2 page 15, line 19 - page 17, line 31 -----	1-9
A	US 4 735 736 A (CHUNG DAVID Y [US]) 5 April 1988 (1988-04-05) column 6, line 60 - column 7, line 60 -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/052015

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
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			US	2009192061	A1	30-07-2009

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