

Description

This invention relates to a novel multi-functional lubricant additive which is a VI improver, a dispersant and an anti-oxidant additive when employed in a lubricating oil composition.

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

U.S. 3,522,180 discloses a method for the preparation of an ethylene-propylene copolymer substrate effective as a viscosity index improver for lubricating oils.

U.S. 4,026,809 discloses graft copolymers of a methacrylate ester and an ethylene-propylene-alkylidene norbornene terpolymer as a viscosity index improver for lubricating oils.

U.S. 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 polyfunctional material reactive with carboxyl groups, such as a polyamine, a polyol, or a hydroxyamine which reaction product is useful as a sludge and varnish control additive in lubricating oils.

U.S. 4,137,185 discloses a stabilized imide graft of an ethylene copolymer additive for lubricants.

U.S. 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 C-vinylpyridine or N-vinylpyrrolidone to provide a dispersant VI improver for lubricating oils.

U.S. 4,320,019 discloses a multipurpose lubricating additive 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. 4,340,689 discloses a process for grafting a functional organic group onto an ethylene copolymer or an ethylene-propylene-diene terpolymer.

U.S. 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 monoamine-polyamine mixture.

U.S. 4,382,007 discloses a dispersant - VI improver prepared by reacting a polyamine-derived dispersant with an oxidized ethylene-propylene polymer or an ethylene-propylene diene terpolymer.

U.S. 4,144,181 discloses polymer additives for fuels and lubricants comprising a grafted copolymer reacted with a polyamine, polyol or hydroxyamine and finally reacted with an alkaryl sulfonic acid.

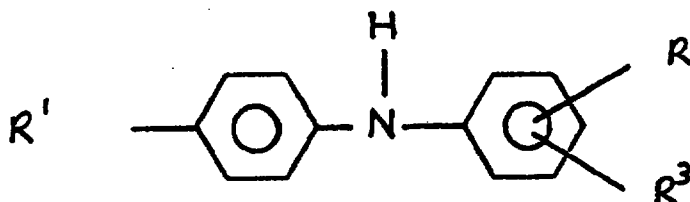
An object of this invention is to provide a novel derivatized graft copolymer composition.

Another object of the invention is to provide a multi-functional lubricant additive effective for imparting viscosity index, dispersancy and anti-oxidant properties to a lubricating oil composition.

A further object is to provide a novel lubricating oil composition containing the graft copolymer additive of the invention as well as to provide concentrates of the novel additive of invention.

The novel reaction product of the invention comprises an ethylene copolymer or terpolymer of a C_3 to C_{10} alpha-monoolefin and optionally a non-conjugated diene or triene on which has been grafted an ethylenically unsaturated carboxylic function which is then further derivatized with an amino-aromatic polyamine compound from the group consisting of:

a) an N-arylphenylenediamine represented by the formula:

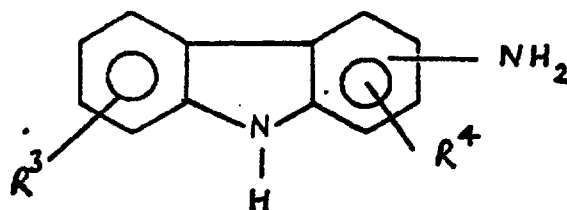


in which R^1 is H, -NHaryl, -NHalkyl, or branched or straight chain radical having from 4 to 24 carbon atoms that can be alkyl, alkenyl, alkoxy, aralkyl, alkaryl, hydroxyalkyl or aminoalkyl,

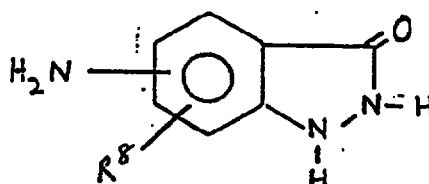
R^2 is NH_2 , $CH_2-(CH_2)_n-NH_2$ or CH_2 -aryl- NH_2 in which n has a value from 1 to 10

R^3 is alkyl, alkenyl, alkoxy, aralkyl, alkaryl, having from 4 to 24 carbon atoms,

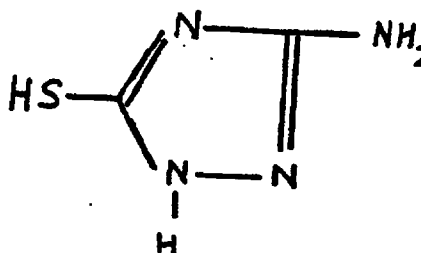
b) an aminocarbazole represented by the formula:



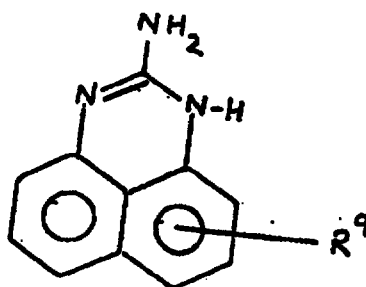
in which R³ and R⁴ represent hydrogen or an alkyl or alkenyl, radical having from 1 to 14 carbon atoms, c) an amino-indazolinone represented by the formula:



in which R⁸ is hydrogen or an alkyl radical having from 1 to 14 carbon atoms d) an aminomercaptotriazole represented by the formula:



e) and an aminoperimidine represented by the formula,



in which R⁹ represents hydrogen or an alkyl radical having from 1 to 14 carbon atoms, and

The novel lubricant of the invention comprises an oil of lubricating viscosity and an effective amount of the novel reaction product. The lubricating oil will be characterized by having viscosity index improver and dispersancy, anti-oxidant properties.

Concentrates of the reaction product of the invention are also contemplated.

The polymer or copolymer substrate employed in the novel additive of the invention may be prepared from ethylene and propylene or it may be prepared from ethylene and a higher olefin within the range of C₃ to C₁₀ alpha-monoolefins.

More complex polymer substrates, often designated as interpolymers, may be prepared using a third component. The third component generally used to prepare an interpolymer substrate is a polyene monomer selected from non-conjugated dienes and trienes. The non-conjugated diene component is one having from 5 to 14 carbon atoms in the chain. Preferably, the diene monomer is characterized by the presence of a vinyl group in its structure and can include cyclic and bi-cyclo compounds. Representative dienes include 1,4-hexadiene, 1,4-cyclohexadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 1,5-heptadiene, and 1,6-octadiene. A mixture of more than one diene can be used in the preparation of the interpolymer. A preferred non-conjugated diene for preparing a terpolymer or interpolymer substrate is 1,4-hexadiene.

The triene component will have at least two non-conjugated double bonds, and up to 30 carbon atoms in the chain. Typical trienes useful in preparing the interpolymer of the invention are 1-isopropylidene-3a,4,7,7a-tetrahydroindene, 1-isopropylidenedicyclopentadiene, dehydro-isodicyclopentadiene, and 2-(2-methylene-4-methyl-3-pentenyl)-[2.2.1] bicyclo-5-heptene.

The polymerization reaction to form the polymer substrate is generally carried out in the presence of a catalyst in a solvent medium. The polymerization solvent may be any suitable inert organic solvent that is liquid under reaction conditions for solution polymerization of monoolefins which is generally conducted in the presence of a Ziegler type catalyst. Examples of satisfactory hydrocarbon solvents include straight chain paraffins having from 5-8 carbon atoms, with hexane being preferred. Aromatic hydrocarbons, preferably aromatic hydrocarbons 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. It is desirable that the solvent be free of substances that will interfere with a Ziegler polymerization reaction.

In a typical preparation of a polymer substrate, hexane is first introduced into a reactor and the temperature in the reactor is raised moderately to about 30°C. Dry propylene is fed to the reactor until the pressure reaches 40-45 inches of mercury (135.5 to 152.4KPa). The pressure is then increased to about 60 inches of mercury (203.2KPa) and dry ethylene and 5-ethylidene-2-norbornene are fed to the reactor. The monomer feeds are stopped and a mixture of aluminum sesquichloride and vanadium oxytrichloride are added to initiate the polymerization reaction. Completion of the polymerization reaction is evidenced by a drop in the pressure in the reactor.

Ethylene-propylene or higher alpha monoolefin copolymers may consist of from 15 to 80 mole percent ethylene and from 20 to 85 mole percent propylene or higher monoolefin with the preferred mole ratios being from 25 to 75 mole percent ethylene and from 25 to 75 mole percent of a C₃ to C₁₀ alpha monoolefin with the most preferred proportions being from 25 to 55 mole percent ethylene and 45 to 75 mole percent propylene.

Terpolymer variations of the foregoing polymers may contain from 0.1 to 10 mole percent of a non-conjugated diene or triene.

The polymer substrate, that is the ethylene copolymer or terpolymer is an oil-soluble, substantially linear, rubbery material having an average molecular weight from 5,000 to 500,000 with a preferred molecular weight range of 25,000 to 250,000 and a most preferred range from 50,000 to 150,000.

The terms polymer and copolymer are used generically to encompass ethylene copolymers, terpolymers or interpolymers. These materials may contain minor amounts of other olefinic monomers so long as their basic characteristics are not materially changed.

An ethylenically unsaturated carboxylic acid material is next grafted onto the prescribed polymer backbone. These materials which are attached to the polymer contain at least one ethylenic bond and at least one, preferably two, carboxylic acid or its anhydride groups or a polar group which is convertible into said carboxyl groups by oxidation or hydrolysis. Maleic anhydride or a derivative thereof is preferred. It grafts onto the ethylene copolymer or terpolymer to give two carboxylic acid functionalities. Examples of additional unsaturated carboxylic materials include chlormaleic anhydride, itaconic anhydride, or the corresponding dicarboxylic acids, such as maleic acid, fumaric acid and their monoesters.

The ethylenically unsaturated carboxylic acid material may be grafted onto the polymer backbone in a number of ways. It may be grafted onto the backbone by a thermal process known as the "ene" process or by grafting in solution or in solid form using a radical initiator. The free-radical induced grafting of ethylenically unsaturated carboxylic acid materials in solvents, such as benzene is a preferred method. It is carried out at an elevated temperature in the range of 100°C. to 250°C, preferably 120° to 190°C and more preferably at 150° to 180°C, e.g. above 160°C, in a solvent, preferably a mineral lubricating oil solution containing, e.g. 1 to 50, preferably 5 to 30 wt.%, based on the initial total oil solution, of the ethylene polymer and preferably under an inert environment.

The free-radical initiators which may be used are peroxides, hydroperoxides, and azo compounds and preferably those which have a boiling point greater than 100°C and decompose thermally within the grafting tem-

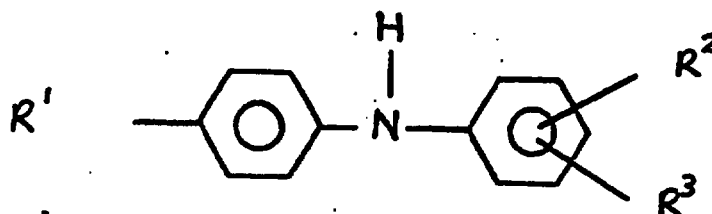
perature range to provide free radicals. Representative of these free-radical initiators are azobutyronitrile and 2,5-dimethyl-hex-3-yne-2,5 bis-tertiary-butyl peroxide. The initiator is used in an amount of between 0.005% and 1% by weight based on the weight of the reaction mixture solution. The grafting is preferably carried out in an inert atmosphere, such as under nitrogen blanketing. The resulting polymer intermediate is characterized by having carboxylic acid acylating functions within its structure.

In the solid or melt process for forming a graft polymer, the unsaturated carboxylic acid with the optional use of a radical initiator is grafted on molten rubber using rubber masticating or shearing equipment. The temperature of the molten material in this process may range from 150-400°C.

Polymer substrates or interpolymers are available commercially. Particularly useful are those containing from 40 to 60 mole percent ethylene units, and 60 to 40 mole percent propylene units. Examples are "Ortholeum 2052" and "PL-1256" available from E.I. duPont deNemours and Co. The former is a terpolymer containing about 48 mole percent ethylene units, 48 mole percent propylene units and 4 mole percent 1,4-hexadiene units, having an inherent viscosity of 1.35. The latter is a similar polymer with an inherent viscosity of 1.95. The viscosity average molecular weights of the two are of the order of 200,000 and 280,000, respectively.

The polymer intermediate possessing carboxylic acid acylating functions is reacted with an amino-aromatic polyamine compound from the group consisting of:

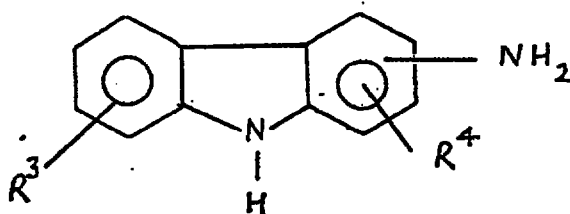
a) an N-arylphenylenediamine represented by the formula:



in which R¹ is hydrogen, -NH-Aryl, -NH-Aralkyl, a branched or straight chain radical having from 4 to 24 carbon atoms that can be alkyl, alkenyl, alkoxy, aralkyl, alkaryl, hydroxyalkyl or aminoalkyl

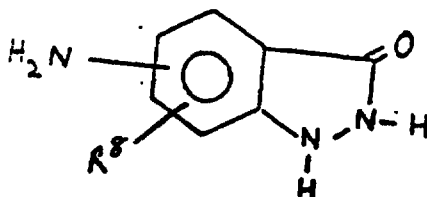
R² is NH₂, CH₂-(CH₂)ₙ-NH₂, CH₂-aryl-NH₂, in which n has a value from 1 to 10, and R³ is alkyl, alkenyl, alkoxy, aralkyl, alkaryl having from 4 to 24 carbon atoms

b) an aminocarbazole represented by the formula:



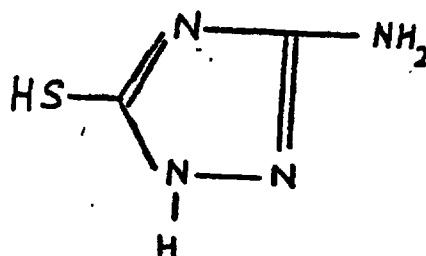
in which R and R¹ represent hydrogen or an alkyl, alkenyl, or alkoxy radical having from 1 to 14 carbon atoms

c) an amino-indazolinone represented by the formula:

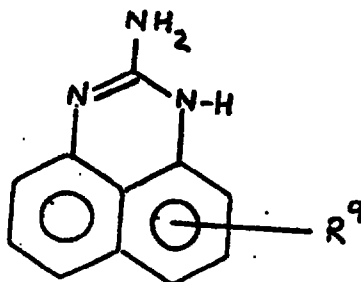


in which R is hydrogen or an alkyl radical having from 1 to 14 carbon atoms

d) an aminomercaptotriazole represented by the formula:



e) an aminoperimidine represented by the formula:



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

Particularly preferred N-arylphenylenediamines are the N-phenylphenylenediamines, for example, N-phenyl-1,4-phenylenediamine, N-phenyl-1,3-phenylenediamine, and N-phenyl-1,2-phenylenediamine.

The reaction between the polymer substrate intermediate having grafted thereon carboxylic acid acylating function and the prescribed amino-aromatic polyamine compound is conducted by heating a solution of the polymer substrate under inert conditions and then adding the amino-aromatic polyamine compound to the heated solution generally with mixing to effect the reaction. It is convenient to employ an oil solution of the polymer substrate heated to 140 to 175°C. while maintaining the solution under a nitrogen blanket. The amino-aromatic polyamine compound is added to this solution and the reaction is effected under the noted conditions.

The following examples illustrate the preparation of the novel reaction product additive of the invention.

Example I

60 grams of a solid maleic anhydride graft polymer (rubber) in which the polymer substrate consisted of about 58 mole percent ethylene and 42 mole percent propylene having an average molecular weight of 80,000 on which has been grafted 1.5 weight percent of maleic anhydride was dissolved in 485 grams of solvent neutral oil at 160°C. with mechanical stirring while the mixture was maintained under a nitrogen blanket. After the rubber polymer had dissolved, mixing was continued for an additional hour at 160°C.

1.85 grams of neat N-phenyl-1,4-phenylenediamine was added to the oil solution of the polymer and a reaction effected over 4 hours at 160°C under nitrogen. The reaction mixture containing the derivatized graft polymer was then cooled and filtered.

Example II

70 grams of a solid maleic anhydride graft polymer rubber in which the polymer substrate consisted of about 58 mole percent ethylene and 42 mole percent propylene having on average molecular weight of 80,000 on which has been grafted 0.7 weight percent of maleic anhydride was dissolved in 513 grams of solvent neutral oil at 160°C. with mechanical stirring while the mixture was maintained under a nitrogen blanket. After the polymer had dissolved, mixing was continued for an additional 3 hours at 160°C.

1.1 grams of neat N-phenyl-1,4-phenylenediamine was added to the oil solution of the polymer and a reaction effected over 3 hours at 160°C under nitrogen. The reaction mixture containing the derivatized graft polymer was cooled and then filtered through a 100 mesh screen.

Example III to VI

Derivatized graft polymers are prepared employing the polymer and procedures shown in Example I employing the following amino-aromatic polyamines

- Example III Aminocarbazole
- Example IV Aminoperimidine
- Example V Aminocaptotriazole
- Example VI N-phenyl-1,3-phenylenediamine

The novel graft and derivatized polymer of the invention is useful as an additive for lubricating oils. They are multi-functional additives for lubricants being effective to provide dispersancy, viscosity index improvement and anti-oxidant properties to lubricating oils. They can be employed in a variety of oils of lubricating viscosity including natural and synthetic lubricating oils and mixtures thereof. The novel additives can be employed in crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines. The compositions can also be used in gas engines, or turbines, automatic transmission fluids, gear lubricants, metal-working lubricants, hydraulic fluids and other lubricating oil and grease compositions. Their use in motor fuel compositions is also contemplated.

The base oil may be a natural oil including liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types.

In general, the lubricating oil composition of the invention will contain the novel reaction product in a concentration ranging from 0.1 to 30 weight percent. A preferred concentration range for the additive is from 1 to 15 weight percent based on the total weight of the oil composition.

Oil concentrates of the additives may contain from 1 to 50 weight percent of the additive reaction product in a carrier or diluent oil of lubricating oil viscosity.

The novel reaction product of the invention may be employed in lubricant compositions together with conventional lubricant additives. Such additives may include additional dispersants, detergents, anti-oxidants, pour point depressants, anti-wear agents and the like.

The novel additive reaction product of the invention was tested for its effectiveness as a dispersant and as an anti-oxidant in a formulated lubricating oil composition. In all of the examples, the polymer substrate was similar comprising about 58 mole percent ethylene, 42 mole percent propylene having an average molecular weight of about 80,000. The base lubricating oil used in the dispersancy test was a typical formulated lubricating oil as represented by the values set forth in Table I.

TABLE I

Component	Parts By Wgt.
Solvent neutral oil A	75.25
Solvent neutral oil B	21.64
Zinc Dialkyldithiophosphate	1.22
4.4'dinonyldiphenylamine	.39
Overbased magnesium sulfonate	1.50
Silicone anifoamant	150 PPM
Product	10
<u>Analyses</u>	
Viscosity Kin 40°C m ² S ⁻¹	30.4 x 10 ⁻⁶
Viscosity Kin 100°C m ² S ⁻¹	5.33 x 10 ⁻⁶
Pour Point, °F. (°C)	+10 (-12)
Ash Sulfated, % D874	0.88
Phosphorus, % X-Ray	0.12
Sulfur, % X-Ray Total	0.32
Zinc, % X-Ray	0.13

oil A had a sp. gr. 60/60°F (15.5/15.5°C) of 0.858-0.868; Vis 100°F (38°C) 123-133 SUS (26 to 29 x 10⁻⁶m²s⁻¹, Pour Point 0°F (-18°C). Oil B had a sp. gr. 60/60°F. (15.5/15.5°C) of 0.871-0.887; Vis. 100°F (38°C) 325-350 SUS (70 to 75 x 10⁻⁶m²s⁻¹; Pour Point +10°F (-12°C). Zinc salt is a salt of mixed alcohols-isopropanol and P₂S₆ product as described in U.S. Pat. No. 3,292,181. The overbased magnesium sulfonate had a TBN of 395 and is a salt of branched C₂₀-C₄₀ monoalkylbenzene sulfuric acid (MW 530-540) together with about 10% magnesium carbonate, 14% magnesium hydroxide and 4% magnesium sulfate.

The dispersant properties of the additive-containing oil are determined in the Bench VC Dispersancy Test (BVCT). Dispersancy of a lubricating oil is determined relative to three references which are the results from three standard blends testing along with the unknown. The test additives were blended into a formulated oil containing no dispersant. The additive reaction product was employed in the oil at a concentration of 1.20 weight percent polymer solution. The numerical value of the test results decreases with an increase in effectiveness.

TABLE II
BENCH VC DISPERANCY TEST

5

	<u>Additive</u>	<u>Result</u>
	Example 1	27
10	Example 2	27
	Ethylene-propylene copolymer	99
	Commercial N-vinylpyrrolidene	
15	grafted dispersant olefin copolymer	29

20 The anti-oxidant properties of the novel reaction product in a lubricating oil was determined in the Bench Oxidation Test. In this test, 1.5 weight percent of the additive reaction product is blended into solvent neutral oil 130(S.U.S. $28 \times 10^{-6} \text{m}^2 \text{s}^{-1}$) at 100°F(38°C). The mixture is continuously stirred while being heated accompanied by bubbling with air. Samples are withdrawn periodically for analysis by Differential Infrared Absorption (DIR) to observe changes in the intensity of the carboxyl vibration band at 1710 cm^{-1} . A low carboxyl vibration band intensity indicates higher thermal-oxidative stability of the sample.

25

TABLE III
BENCH OXIDATION TEST

	<u>Additive</u>	<u>Result</u>
	Example I	3
30	Example II	10
	Ethylene-propylene copolymer (EPM)	15
35	Maleic anhydride grafted (EPM)	27
	Commercial N-vinylpyrrolidene	
	grafted dispersant olefin	
40	Copolymer (DOCP)	15

45 The test results for Example I and II demonstrate substantial improvements in anti-oxidant properties due to incorporation of the novel reaction product of the invention in an oil composition as compared to the results obtained from known VI and dispersant VI improvers. The result for Example I was particularly outstanding.

50 The novel polymers may also be characterized as deposit protection agents as measured by the Single Cylinder CEC MWM-B Diesel Engine Test (DIN 51361 Parts I, II, and IV). In this test, a solution (8.5 wt. %) of polymer in SNO-100 oil is blended into a fully formulated oil which does not contain a VI improver. Results are presented in "Merits", a higher merit evidencing better protection against deposits. The results are set forth in Table IV below.

55

TABLE IV
ENGINE TEST PERFORMANCE

Engine Tests	VI Improvers		
	NVP-EPM	DMAPA/ MA-EPM	Example I
MWM-B. SAE 15w-40 MO			
Merits	53	59	63
Sequence VI. SAE 5w-30 MO			
Avg. Sludge	6.4	7.6	8.8
Avg. Varnish	5.2	6.2	6.8
Piston Skirt Varnish	6.9	7.0	7.6
Cam Lobe Wear, Mils (μm)			
Max	19.2 (488)	9.7 (246)	6.5 (165)
Avg.	4.8 (122)	7.9 (201)	2.3 (58)

NVP-EPM = N-Vinyl pyrrolidone grafted ethylene propylene copolymer

DMAPA/MA-EPM: Maleic Anhydride grafted ethylene propylene copolymer derivatized with N-dimethylaminopropylamine.

The motor oil composition containing reaction product of Example I exhibited outstanding engine cleanliness as compared to known grafted and derivatized polymers.

Claims

1. A method for preparing a lubricant additive composition by reacting a polymer comprising from 15 to 80 mole percent of ethylene, from 20 to 85 mole percent of a C_3 - C_{10} alpha-monoolefin, and from 0 to 15 mole percent of a polyene selected from non-conjugated dienes and trienes said polymer having an average molecular weight of 5,000 to 500,000 with at least one olefinic carboxylic acid acylating agent to form one or more reaction intermediates having a carboxylic acid acylating function within their structure, and reacting said reaction intermediate with a polyfunctional material reactive with carboxyl groups, characterised in that the polyfunctional material is an amino-aromatic polyamine compound selected from

a) an N-arylphenylenediamine having the formula:

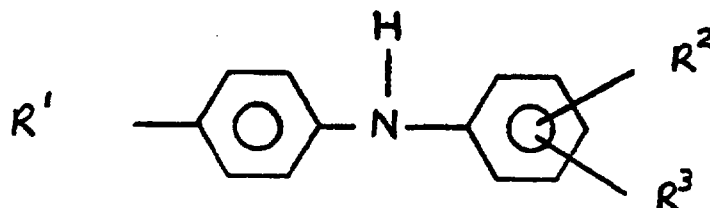




TABLE IV
ENGINE TEST PERFORMANCE

Engine Tests	VI Improvers		
	NVP-EPM	DMAPA/ MA-EPM	Example I
<u>MWM-B. SAE 15w-40 MO</u>			
<u>Merits</u>	53	59	63
<u>Sequence VE. SAE 5w-30 MO</u>			
Avg. Sludge	6.4	7.6	8.8
Avg. Varnish	5.2	6.2	6.8
Piston Skirt Varnish	6.9	7.0	7.6
Cam Lobe Wear, Mils (μm)			
Max	19.2 (488)	9.7 (246)	6.5 (165)
Avg.	4.8 (122)	7.9 (201)	2.3 (58)

NVP-EPM = N-Vinyl pyrrolidone grafted ethylene propylene copolymer

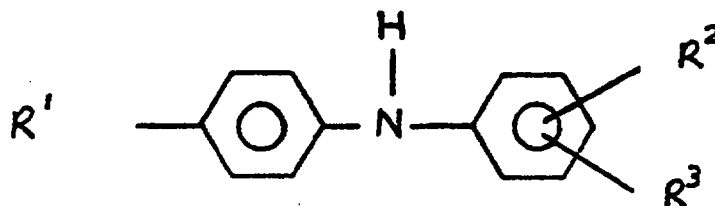
DMAPA/MA-EPM: Maleic Anhydride grafted ethylene propylene copolymer derivatized with N-dimethylaminopropylamine.

The motor oil composition containing reaction product of Example I exhibited outstanding engine cleanliness as compared to known grafted and derivatized polymers.

Claims

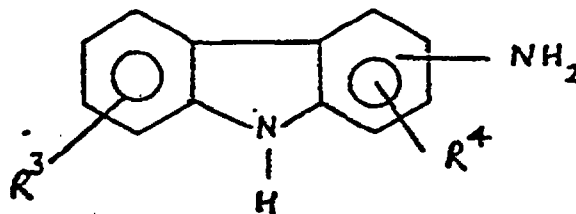
1. A method for preparing a lubricant additive composition by reacting a polymer comprising from 15 to 80 mole percent of ethylene, from 20 to 85 mole percent of a C_3 - C_{10} alpha-monoolefin, and from 0 to 15 mole percent of a polyene selected from non-conjugated dienes and trienes said polymer having an average molecular weight of 5,000 to 500,000 with at least one olefinic carboxylic acid acylating agent to form one or more reaction intermediates having a carboxylic acid acylating function within their structure, and reacting said reaction intermediate with a polyfunctional material reactive with carboxyl groups, characterised in that the polyfunctional material is an amino-aromatic polyamine compound selected from

a) an N-aryphenylenediamine having the formula:

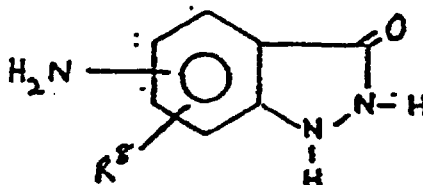




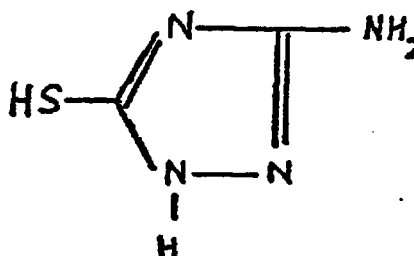
in which R^1 is hydrogen, NH-aryl, NH-alkyl, or a branched or straight chain group having 4 to 24 carbon atoms that can be alkyl, alkenyl, alkoxy, aralkyl, alkaryl hydroxyalkyl or aminoalkyl, R^2 is NH_2 , $CH_2-(CH_2)_n-NH_2$, or CH_2 -aryl- NH_2 in which n is 1 to 10, and R^3 is alkyl, alkenyl, alkoxy, aralkyl, or alkaryl having 4 to 24 carbon atoms,
b) an aminocarbazole having the formula:



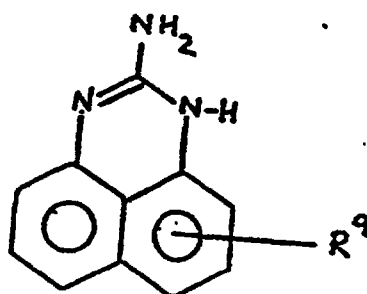
in which R^3 and R^4 are each hydrogen or alkyl or alkenyl, having 1 to 14 carbon atoms,
c) an amino-indazole having the formula:



in which R^6 is hydrogen or alkyl having 1 to 14 carbon atoms,
d) an aminomercaptotriazole having the formula:



and
e) an aminoperimidine having the formula:



in which R^9 is hydrogen or alkyl, alkenyl, or alkoxy having 1 to 8 carbon atoms.



2. A method according to Claim 1 characterised in that the polymer has an average molecular weight from 25,000 to 250,000.

3. A method according to Claim 1 or 2 characterised in that the polymer comprises from 25 to 75 mole percent of ethylene and from 25 to 75 mole percent of a C_3 to C_8 α -monoolefin.

4. A method according to any one of Claims 1 to 3 characterised in that the polymer comprises 0.1 to 10 mole percent of a polyene.

5. A method according to any one of Claims 1 to 4 characterised in that the olefinic carboxylic acid acylating agent is maleic anhydride or itaconic anhydride.

6. A method according to any one of Claims 1 to 5 characterised in that the amino-aromatic polyamines is an N-phenylphenylenediamine or aminothiazole.

7. A method according to any one of Claims 1 to 5 characterised in that the amino-aromatic polyamine is N-phenyl-1, 4-phenylene diamine or N-phenyl-1, 3-phenylene diamine.

8. A lubricating oil composition comprising 70-99.9 wt% of an oil of lubricating viscosity and 0.1-30 wt%, based on the total weight of the oil composition of an additive composition prepared by a method according to any one of Claims 1 to 7.

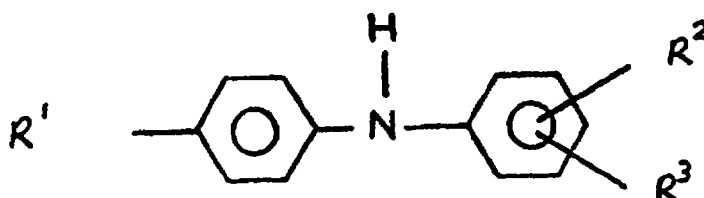
9. A concentrate for a lubricating oil comprising a diluent oil of lubricant viscosity and from 1 to 50 weight percent, based on the total weight of the concentrate, of an additive composition prepared by a method according to any one of Claims 1 to 7.

10. The used of from 0.1 to 30 weight percent, based on the total weight of the oil composition of a lubricant additive composition prepared according to the method defined in any one of Claims 1 to 7 as an antioxidant additive in a lubricating oil composition comprising 70 - 99.9 weight percent of an oil of lubricating viscosity.

Patentansprüche

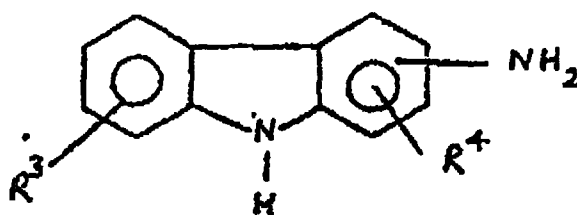
1. Verfahren zur Herstellung einer Schmiermitteladditivzusammensetzung durch Umsetzen eines Polymers, das von 15 bis 80 Mol-% Ethylen, von 20 bis 85 Mol-% eines C_3 - C_{10} - α -Monoolefins und von 0 bis 15 Mol-% eines aus nicht-konjugierten Dienen und Trienen ausgewählten Polyens umfaßt, wobei besagtes Polymer ein mittleres Molekulargewicht von 5000 bis 500.000 aufweist, mit wenigstens einem Acylierungsmittel auf der Basis einer olefinischen Carbonsäure, um eine oder mehrere Reaktionszwischenprodukte mit einer Carbonsäure-Acylierungsfunktion in ihrer Struktur zu bilden, und Umsetzen besagten Reaktionszwischenproduktes mit einem mit Carboxylgruppen reaktiven polyfunktionalen Material, dadurch gekennzeichnet, daß das polyfunktionale Material eine aminoaromatische Polyaminverbindung ist, ausgewählt aus

a) einem N-Arylphenylen-diamin mit der Formel



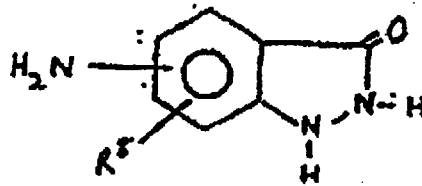
in der R^1 Wasserstoff, NH-Aryl, NH-Alkyl oder eine verzweigte oder geradkettige Gruppe mit 4 bis 24 Kohlenstoffatomen ist, die Alkyl, Alkenyl, Alkoxy, Aryl, Alkaryl, Hydroxyalkyl oder Aminoalkyl sein kann, R^2 NH_2 , $CH_2-(CH_2)_n-NH_2$ oder CH_2 -Aryl- NH_2 ist, wobei n 1 bis 10 ist, und R^3 Alkyl, Alkenyl, Alkoxy, Aryl oder Alkaryl mit 4 bis 24 Kohlenstoffatomen ist,

b) einem Aminocarbazol mit der Formel :

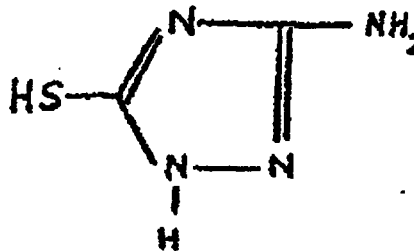




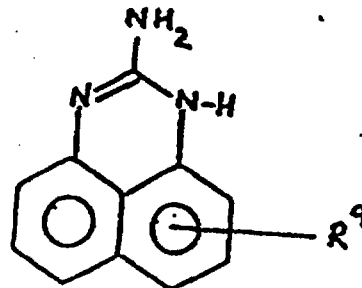
in der R³ und R⁴ jeweils Wasserstoff oder Alkyl oder Alkenyl sind, mit 1 bis 14 Kohlenstoffatomen,
c) einem Aminoindazolinon mit der Formel:



in der R⁸ Wasserstoff oder Alkyl mit 1 bis 14 Kohlenstoffatomen ist,
d) einem aminomercaptotriazol mit der Formel :



und
e) einem Aminoperimidin mit der Formel :



in der R⁹ Wasserstoff oder Alkyl, Alkenyl oder Alkoxy mit 1 bis 8 Kohlenstoffatomen ist.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Polymer ein mittleres Molekulargewicht von 25.000 bis 250.000 besitzt.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Polymer von 25 bis 75 Mol-% Ethylen und von 25 bis 75 Mol-% eines C₃-C₈- α -Monoolefins umfaßt.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Polymer 0,1 bis 10 Mol-% eines Polyens umfaßt.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Acylierungsmittel auf der Basis einer olefinischen Carbonsäure Maleinsäureanhydrid oder Itaconsäureanhydrid ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das aminoaromatische Polyamin ein N-Phenyl-phenylendiamin oder Amino-thiazol ist.

7. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das aminoaromatische Polyamin N-Phenyl-1,4-phenylendiamin oder N-Phenyl-1,3-phenylendiamin ist.

8. Schmierölzusammensetzung, die 70-99,9 Gew.-% eines Öls mit schmierender Viskosität und 0,1-30 Gew.-%, bezogen auf das Gesamtgewicht des Öls, einer Additivzusammensetzung umfaßt, die nach einem Verfahren nach einem der Ansprüche 1 bis 7 hergestellt ist.

9. Konzentrat für ein Schmieröl, das ein Verdünnungsöl mit schmierender Viskosität und von 1-50 Gew.-%, bezogen auf das Gesamtgewicht des Konzentrats, einer Additivzusammensetzung umfaßt, die nach einem Verfahren nach einem der Ansprüche 1 bis 7 hergestellt ist.

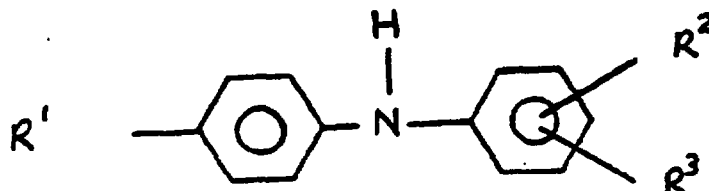


10. Verwendung von 0,1 bis 30 Gew.-%, bezogen auf das Gesamtgewicht der Ölzusammensetzung, einer Schmiermitteladditivzusammensetzung, hergestellt nach dem in einem der Ansprüche 1 bis 7 definierten Verfahren, als ein als Antioxidationsmittel geeignetes Additiv in einer Schmierölzusammensetzung, die 70-99,9 Gew.-% eines Öls mit schmierender Viskosität umfaßt.

Revendications

1. Procédé de préparation d'une composition d'additifs pour lubrifiants par réaction d'un polymère comprenant de 15 à 80 moles % d'éthylène, de 20 à 85 moles % d'une alpha-monooléfine en C₃ à C₁₀ et de 0 à 15 moles % d'un polyène choisi parmi des diènes et triènes non conjugués, ce polymère ayant une masse moléculaire moyenne de 5 000 à 500 000, avec au moins un agent d'acylation d'acide carbonique oléfinique pour former un ou plusieurs intermédiaires de réaction ayant une fonction acylante d'acide carboxylique dans leur structure, et réaction de cet intermédiaire de réaction avec une matière polyfonctionnelle réagissant avec les groupes carboxyle, caractérisé en ce que la matière polyfonctionnelle est une polyamine amino-aromatique choisie parmi

a) une N-arylphénylènediamine répondant à la formule :

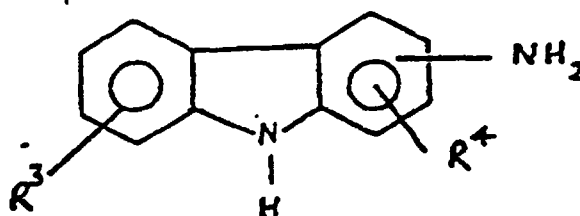


dans laquelle R¹ est un atome d'hydrogène, un groupe NH-aryle, NH-aralkyle, ou un groupe à chaîne linéaire ou ramifiée ayant de 4 à 24 atomes de carbone qui peut être un groupe alkyle, alcényle, alcoyle, aralkyle, alkarylé, hydroxyalkyle ou aminoalkyle,

R² est NH₂, CH₂-(CH₂)_n-NH₂, ou CH₂-aryl-NH₂ où n est un nombre de 1 à 10,

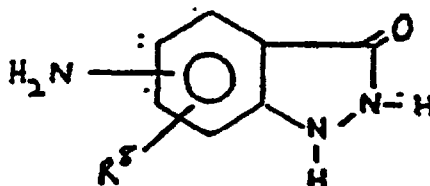
et R³ est un groupe alkyle, alcényle, alcoyle, aralkyle ou alkarylé ayant de 4 à 24 atomes de carbone,

b) un aminocarbazole répondant à la formule :



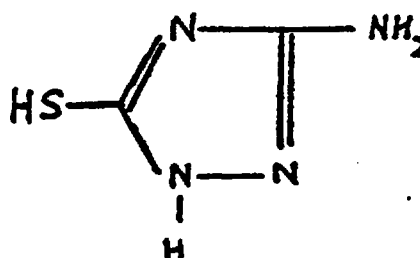
dans laquelle R³ et R⁴ sont chacun un atome d'hydrogène ou un groupe alkyle ou alcényle ayant de 1 à 14 atomes de carbone,

c) une amino-indazolinone répondant à la formule :



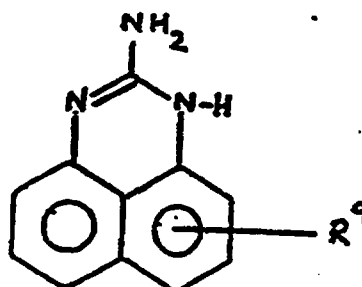
dans laquelle R⁵ est un atome d'hydrogène ou un groupe alkyle ayant de 1 à 14 atomes de carbone,

d) un aminomercaptotriazole répondant à la formule :



et

e) une aminopyrimidine répondant à la formule :



dans laquelle R⁹ est un atome d'hydrogène ou un groupe alkyle, alcényle ou alcoyle ayant de 1 à 8 atomes de carbone.

2. Procédé selon la revendication 1, caractérisé en ce que le polymère a une masse moléculaire de 25 000 à 250 000.

3. Procédé selon les revendications 1 ou 2, caractérisé en ce que le polymère comprend 25 à 75 moles % d'éthylène et 25 à 75 moles % d'une alpha-monooléfine en C₃ à C₈.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que le polymère comprend 0,1 à 10 moles % d'un polyène.

5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que l'agent d'acylation d'acide carboxylique oléfinique est l'anhydride maléique ou l'anhydride itaconique.

6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que la polyamine amino-aromatique est la N-phénylphénylènediamine ou l'aminothiazole.

7. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que la polyamine amino-aromatique est la N-phényl-1, 4-phénylène diamine ou la N-phényl-1, 3-phénylène diamine.

8. Composition d'huile lubrifiante comprenant 70-99,9 % en poids d'une huile de viscosité lubrifiante et 0,1-30 % en poids par rapport au poids total de la composition d'huile, d'une composition d'additif préparée par un procédé selon l'une quelconque des revendications 1 à 7.

9. Concentré pour une huile lubrifiante comprenant une huile de viscosité lubrifiante comme diluant et de 1 à 50 % en poids, par rapport au poids total du concentré, d'une composition d'additif préparée par un procédé selon l'une quelconque des revendications 1 à 7.

10. Utilisation de 0,1 à 30 % en poids, par rapport au poids total de la composition d'huile, d'une composition d'additif pour lubrifiant préparée conformément au procédé défini dans une quelconque des revendications 1 à 7 comme additif anti-oxydant dans une composition d'huile lubrifiante comprenant 70 à 99,9 % en poids d'une huile de viscosité lubrifiante.