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(54) ADDITIF DISPERSIF ET ANTI-OXYDANT ET COMPOSE D'HUILE LUBRIFIANTE CONTENANT CET ADDITIF

(54) DISPERSANT AND ANTI-OXIDANT ADDITIVE AND LUBRICATING OIL COMPOSITION CONTAINING SAME

(57) Disclosed are an additive composition comprising a graft and amine-derivatized copolymer prepared from ethylene and at least one C_3-C_{10} alpha-monoolefin and, optionally, a polyene selected from non-conjugated dienes and trienes comprising from about 15 to 80 mole percent of ethylene, from about 20 to 85 mole percent of the C_3-C_{10} alpha-monoolefin and from about 0 to 15 mole percent of the polyene having an average molecular weight ranging from about 1,000 to 40,000 which has been reacted with at least one olefinic carboxylic acid acylating agent to form one or more acylating reaction intermediates characterized by having at least about 1.5 weight percent of a carboxylic acid acylating function within their structure and reacting the reaction intermediate with an amino-aromatic polyamine compound from the group consisting of an N-arylphenylenediamine, an aminothiazole, an aminocarbazole, an aminoindole, an aminopyrrole, an amino-indazolinone, an aminomercaptotriazole, and an aminoperimidine to form the graft and amine-derivatized copolymer, and a lubricating oil composition containing same.

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DISPERSANT AND ANTI-OXIDANT ADDITIVE AND LUBRICATING OIL COMPOSITION CONTAINING SAME

ABSTRACT

Disclosed are an additive composition comprising a graft and amine-derivatized copolymer prepared from ethylene and at least one C_3-C_{10} alpha-monoolefin and, optionally, a polyene selected from non-conjugated dienes and trienes comprising from about 15 to 80 mole percent of ethylene, from about 20 to 85 mole percent of the C_3-C_{10} alpha-monoolefin and from about 0 to 15 mole percent of the polyene having an average molecular weight ranging from about 1,000 to 40,000 which has been reacted with at least one olefinic carboxylic acid acylating agent to form one or more acylating reaction intermediates characterized by having at least about 1.5 weight percent of a carboxylic acid acylating function within their structure and reacting the reaction intermediate with an amino-aromatic polyamine compound from the group consisting of an N-arylphenylenediamine, an aminothiazole, an aminocarbazole, an aminoindole, an aminopyrrole, an amino-indazolinone, an aminomercaptotriazole, and an aminoperimidine to form the graft and amine-derivatized copolymer, and a lubricating oil composition containing same.

DISPERSANT AND ANTI-OXIDANT ADDITIVE AND LUBRICATING OIL COMPOSITION CONTAINING SAME

(D#79,173 -F)

Background of the Invention

This invention relates to a novel bi-functional lubricant additive which provides dispersancy and anti-oxidant properties when employed in a single grade lubricating oil composition.

Disclosure Statement

Ethylene-propylene copolymers and ethylene-alpha olefin non-conjugated diene terpolymers which have been grafted and derivatized to provide valuable properties in lubricating oil compositions are well known.

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. Pat. No. 4,026,809 dicloses graft copolymers of a methacrylate ester and an ethylene-propylene-alkylidene norbornene terpolymer as a viscosity index improver for lubricating oils.

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

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

U.S. Pat. No. 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. 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 monoamine-polyamine mixture.

U.S. Pat No. 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. 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.

U.S. Pat. No. 4,863,623 discloses multi-functional grafted and derivatized copolymers which provide viscosity index improvement, dispersancy and anti-oxidant properties in a multi-grade lubricating oil composition.

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

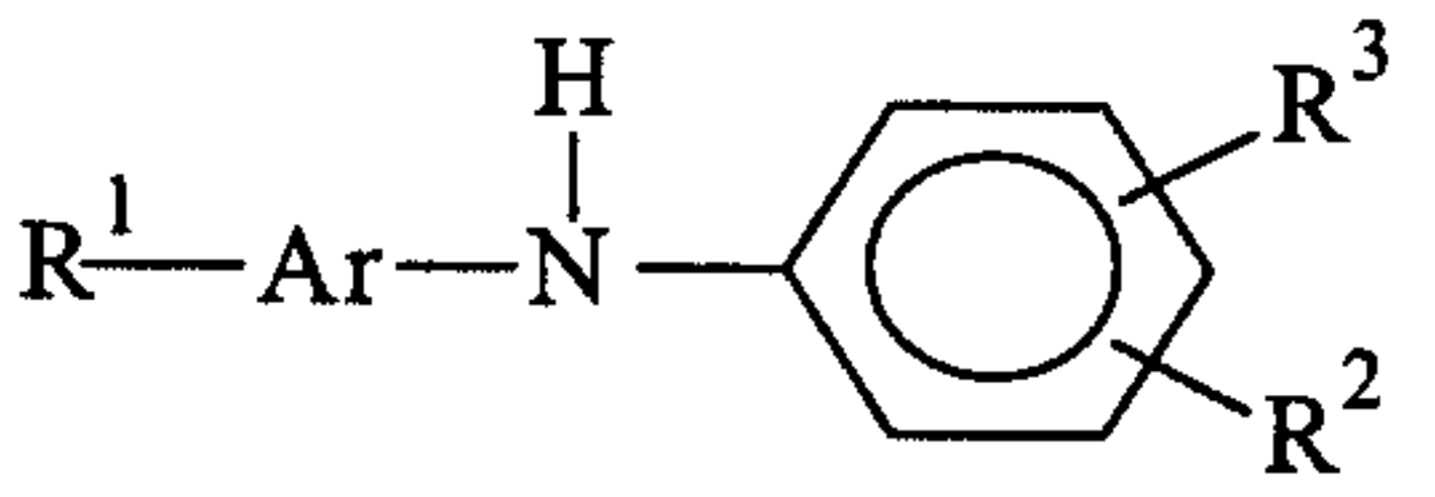
Another object of the invention is to provide a bi-functional lubricant additive effective for imparting dispersancy and anti-oxidant properties to a single grade lubricating oil composition.

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.

Summary of the 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, having a molecular weight ranging from about 1,000 to 40,000 on which has been grafted an ethylenically unsaturated carboxylic function in the amount of at least 1.5 weight percent which is then further derivatized with an amino-aromatic polyamine compound selected from the group consisting of:

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



(I)

in which:

Ar is aromatic,

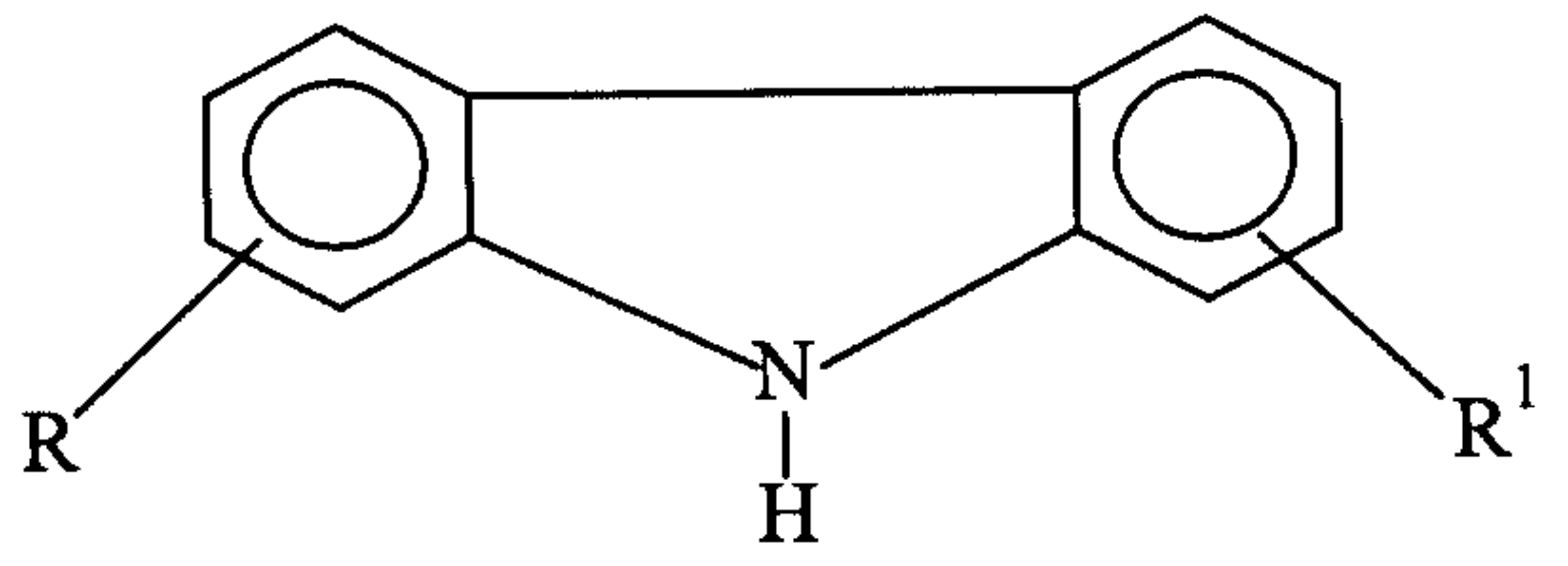
R^1 is H, -NHaryl, -NHarylalkyl or a branched or straight chain radical having from 4 to 24 carbon atoms that can be an alkyl, alkenyl, alkoxy, aralkyl alkaryl, hydroxyalkyl or aminoalkyl group,

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

R^3 is hydrogen or an alkyl, alkenyl, alkoxy, aralkyl or alkaryl group each having from 4 to 24 carbon atoms,

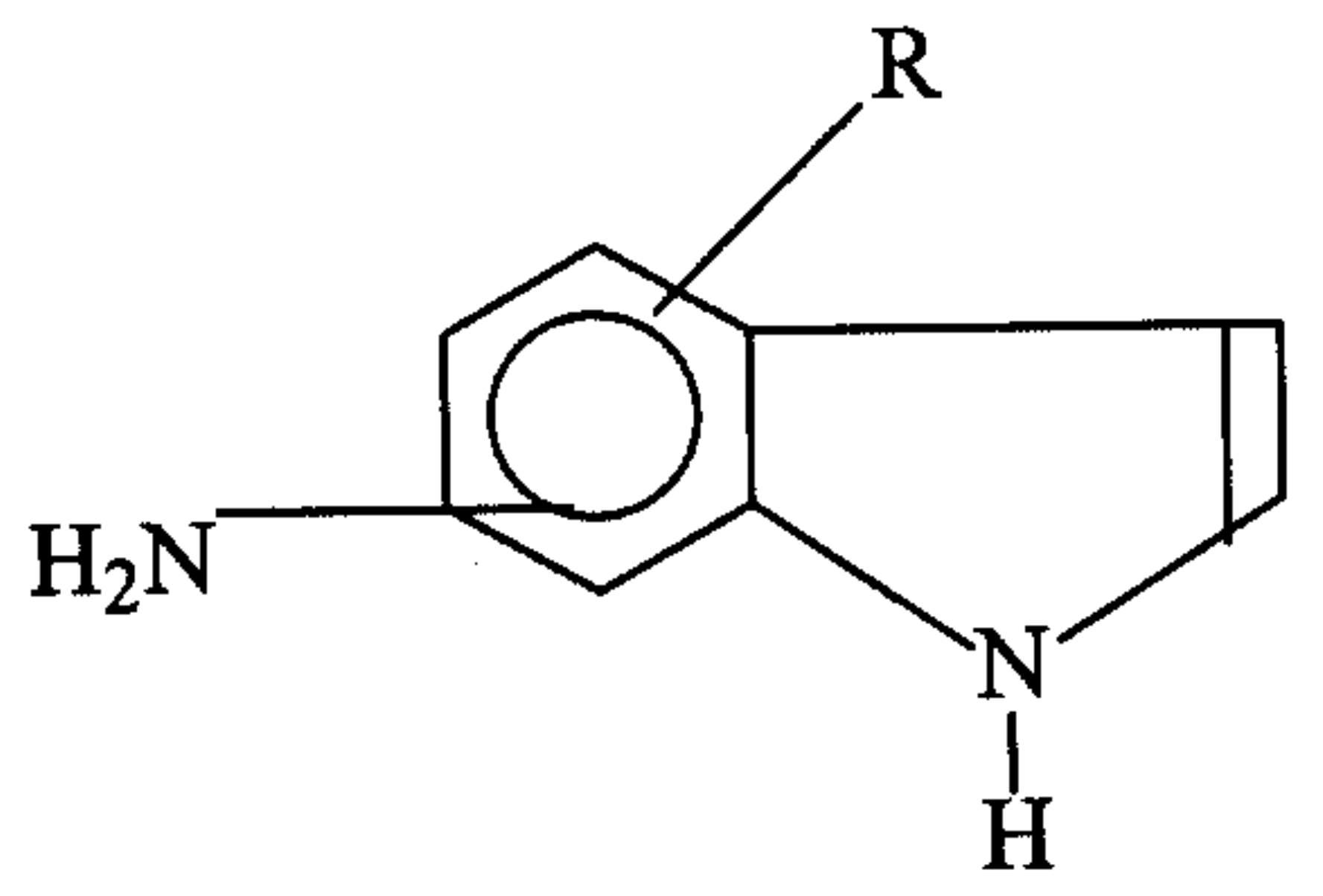
(b) an aminothiazole selected from the group consisting of aminothiazole, aminobenzothiazole, aminobenzothiadiazole and aminoalkylthiazole,

(c) an aminocarbazole represented by the formula:



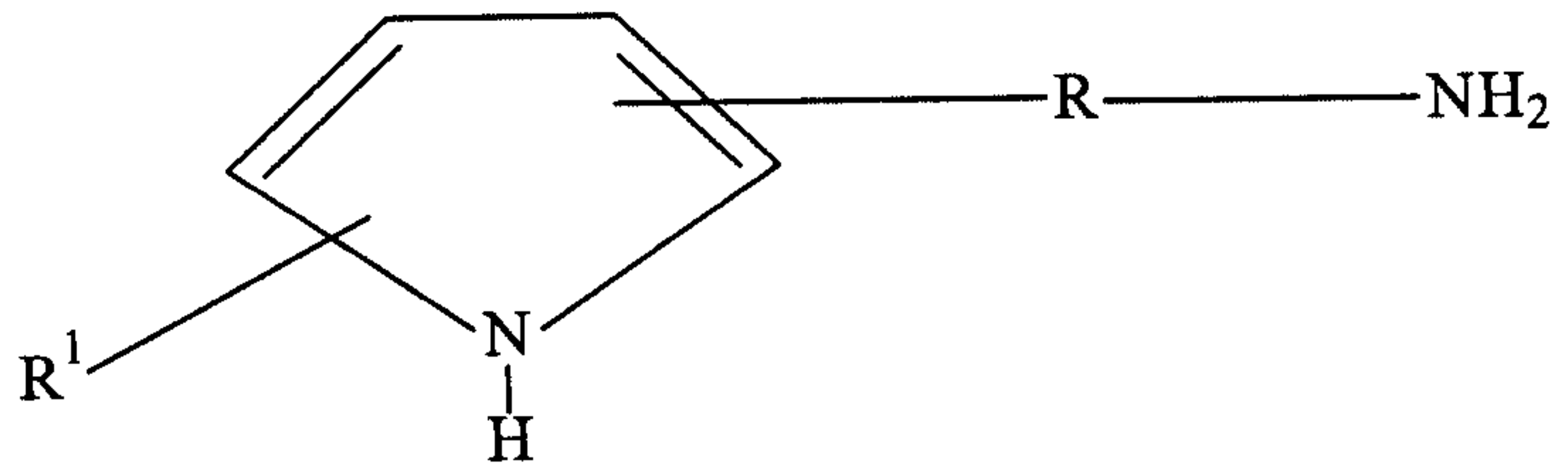
in which R and R^1 each represent hydrogen or an alkyl or alkenyl radical having from 1 to 14 carbon atoms,

(d) an aminoindole represented by the formula:



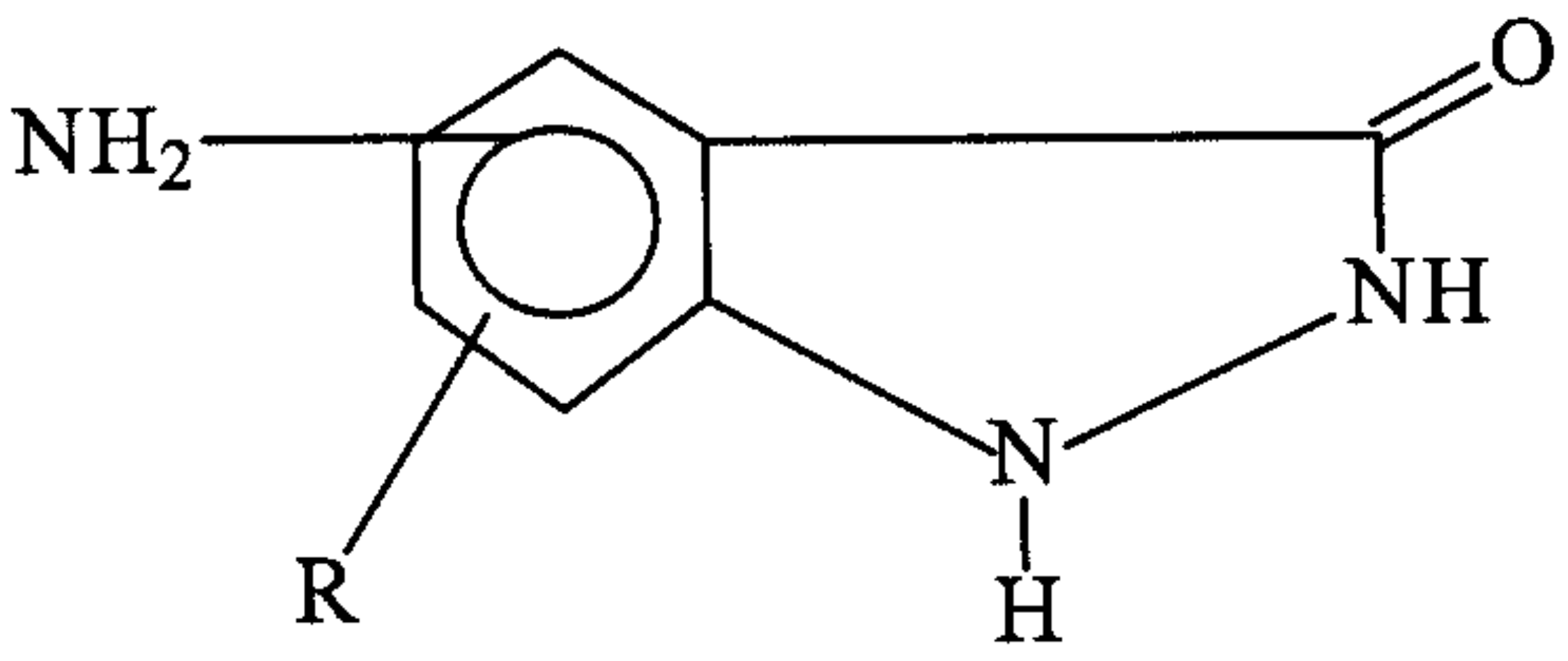
in which R represents hydrogen or an alkyl radical having from 1 to 14 carbon atoms,

(e) an aminopyrrole represented by the formula:



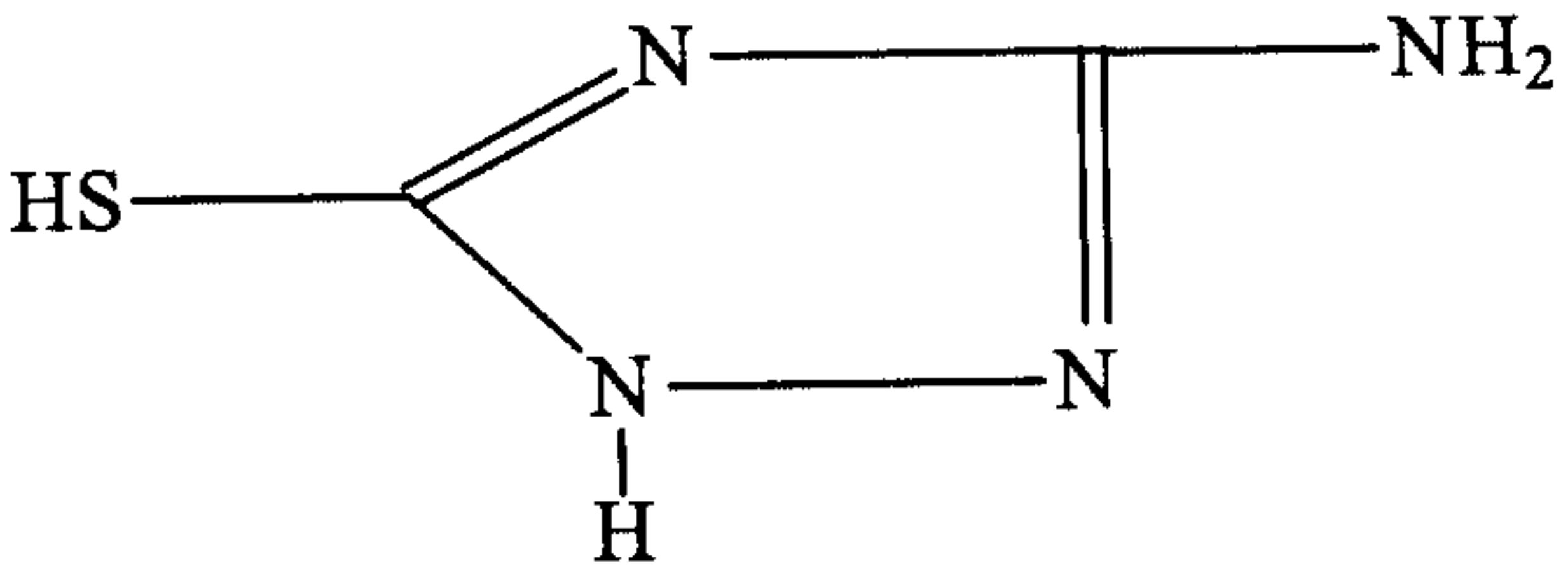
in which R is a divalent alkylene radical having 2-6 carbon atoms and R^1 is hydrogen or an alkyl radical having from 1 to 14 carbon atoms,

(f) an aminoindazolinone represented by the formula:



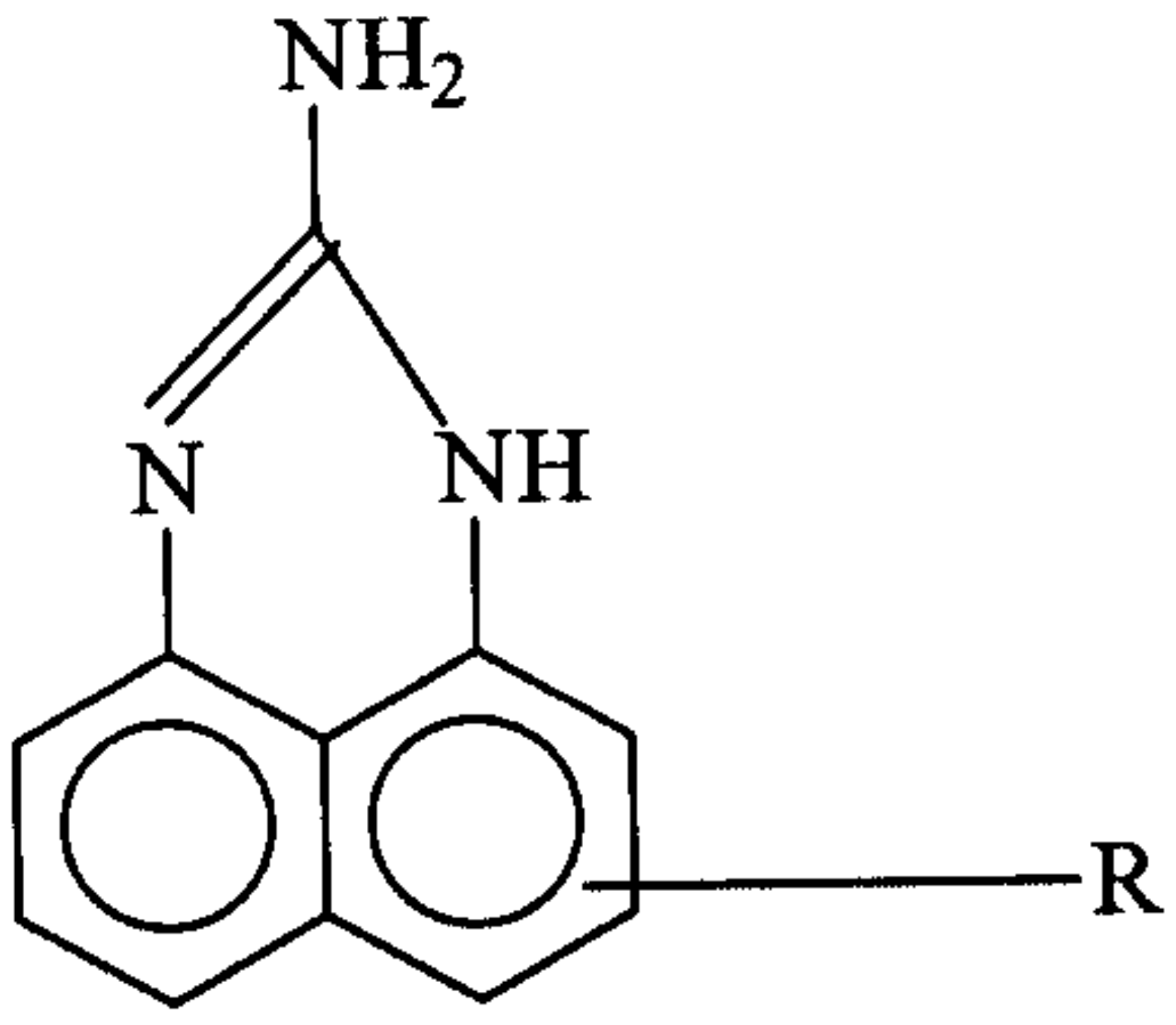
in which R is hydrogen or an alkyl radical having from 1 to 14 carbon atoms,

(g) an aminomercaptotriazole represented by the formula:



, and

(h) an aminopermidine represented by the formula:



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

The novel lubricant of the invention comprises an oil of lubricating viscosity and an effective dispersant and anti-oxidant amount of the novel reaction product. This unique product is characterized as a single grade lubricating oil composition.

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

DETAILED DESCRIPTION OF THE INVENTION

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 C_3 to C_{10} 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-norborene, 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 of interpolymer substrate is 1,4-hexadiene.

The triene component will have at least two non-conjugated double bonds, and up to about 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 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 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 about 40-45 inches of mercury. The pressure is then increased to about 60 inches of mercury 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 about 15 to 80 mole percent ethylene and from about 20 to 85 mole percent propylene or higher monoolefin with the preferred mole ratios being from about 25 to 75 mole percent ethylene and from about 25 to 75 mole percent of a C_3 to C_{10} alpha monoolefin with the most preferred proportions being from 25 to 55 mole percent ethylene and 45 to 75 mole percent propylene.

* Trade-mark

Terpolymer variations of the foregoing polymers may contain from about 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 a number average molecular weight from about 1,000 to 40,000 with a preferred molecular weight range of 5,000 to 20,000 and a most preferred range from about 8,000 to 17,000. The molecular weight of the polymer substrate is determined as number average molecular weight.

It will be appreciated that many polymerization processes produce high molecular weight polymers having molecular weights substantially above 75,000 and commonly ranging from 100,000 to 300,000 molecular weight and above. These high molecular weight polymers which inherently provide viscosity index improvement properties in lubricating oil compositions are not suitable as substrates for the present invention which is intended to provide a dispersant-anti-oxidant additive for single grade motor oil compositions. The high molecular weight polymer substrates must be degraded, usually mechanically or thermally, to the prescribed molecular weight range.

Low molecular weight ethylene copolymer substrates having molecular weights ranging from 1,000 to 40,000 and, more particularly, from about 5,000 to 20,000 molecular weight suitable for preparing the reaction product of the invention are not available commercially. High molecular weight polymer substrates or interpolymers are available commercially such as those containing from about 40 to about 60 mole percent ethylene units and about 60 to about 40 mole percent propylene units. Examples are "Ortholeum 2052*" and "PL-1256*" available

* Trade-mark

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 these polymers are on the order of 200,000 and 280,000, respectively. As previously noted, these are not suitable for a single grade lubricating oil and must be degraded until the polymer is within the prescribed molecular weight range.

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 ethylenically unsaturated bond and at least one, preferably two, carboxylic acid or its anhydride groups or a polar group which is convertible into the 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 other unsaturated carboxylic materials include chlormaleic anhydride, itaconic anhydride, or the corresponding dicarboxylic acids, such as maleic acid, fumaric acid and their monoesters.

The amount of the carboxylic acid material that is grafted onto the prescribed polymer backbone is critical. This amount should be at least 1.5 weight percent of carboxylic acid material on the polymer backbone. It is preferable that the carboxylic acid material amount to 2.5 percent or higher based on the total weight of the grafted polymer. In general, the carboxylic acid material should constitute from 1.5 to 5 weight percent of the grafted polymer backbone with the preferred range being from about 2.25 to 3 weight percent.

The ethylenically unsaturated carboxylic acid material may be grafted onto the polymer backbone in a number of ways. It may be incorporated onto an unsaturated backbone by a thermal process known as the "ene" process or by grafting onto saturated or unsaturated polymer backbone in solution or in solid form using a radical initiator. The free-radical induced grafting of ethylenically unsaturated carboxylic acid materials is preferably done using a mechanical or thermal shearing technique. It is carried out at an elevated temperature in the range of about 100°C to 250°C, preferably 120°C to 190°C and more preferably at 150°C to 180°C.

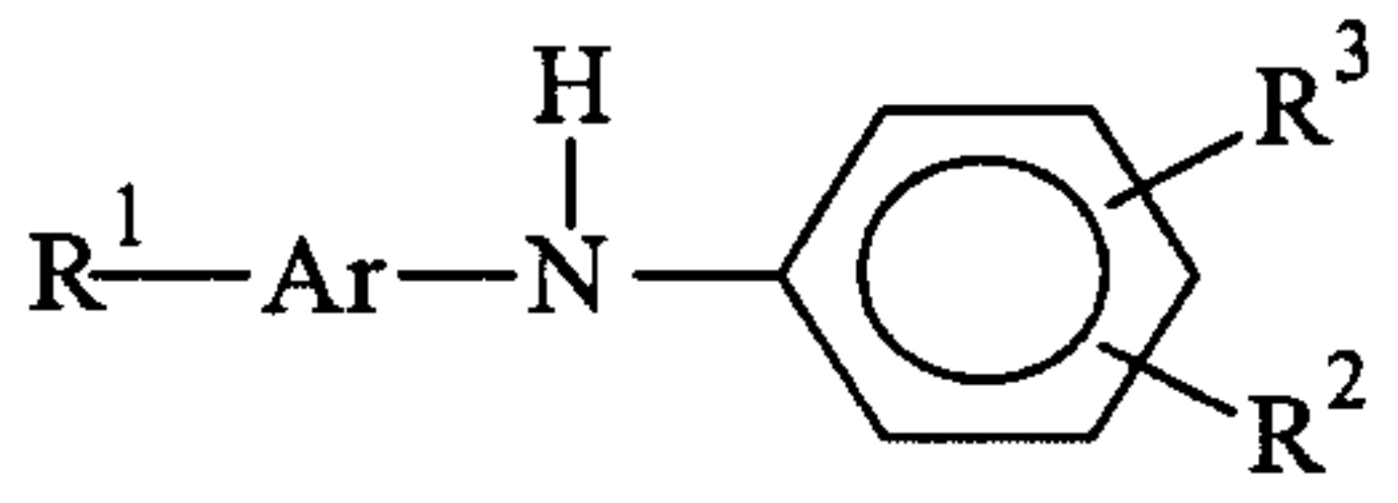
The free-radical initiators which may be used are peroxides, hydroperoxides, and azo compounds and preferably those which have a boiling point greater than about 100°C and decompose thermally within the grafting temperature range to provide free radicals. Representative of these free-radical initiators are azobutyronitrile and 2,5-dimethyl-hex-3-yne-2,5 bis-tertiary-butyl peroxide. The initiator is used in an amount of between about 0.005% and about 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 about 150°C-400°C. Preferably, the melt process is carried out in an extruder.

The preparation of the grafted copolymer intermediate may be conducted in a number of ways. A high molecular weight copolymer may be degraded to the prescribed molecular weight range by a mechanical shearing or thermal process and then reacted with the carboxylic acid material according to known procedures. Alternatively, the high molecular weight copolymer may be grafted with the carboxylic acid material and the resultant grafted copolymer then subjected to a degrading process, e.g. mechanical shearing or thermal shearing to produce a grafted copolymer having the prescribed molecular weight. In still another procedure, a high molecular weight copolymer and the carboxylic acid material may be mixed together and simultaneously reacted under conditions that degrade the copolymer, i.e. by effecting mechanical or thermal shearing while effecting the grafting reaction.

The polymer intermediate possessing carboxylic acid acylating functions is reacted with the amino-aromatic polyamine compound described above. Examples of preferred polyamines include:

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

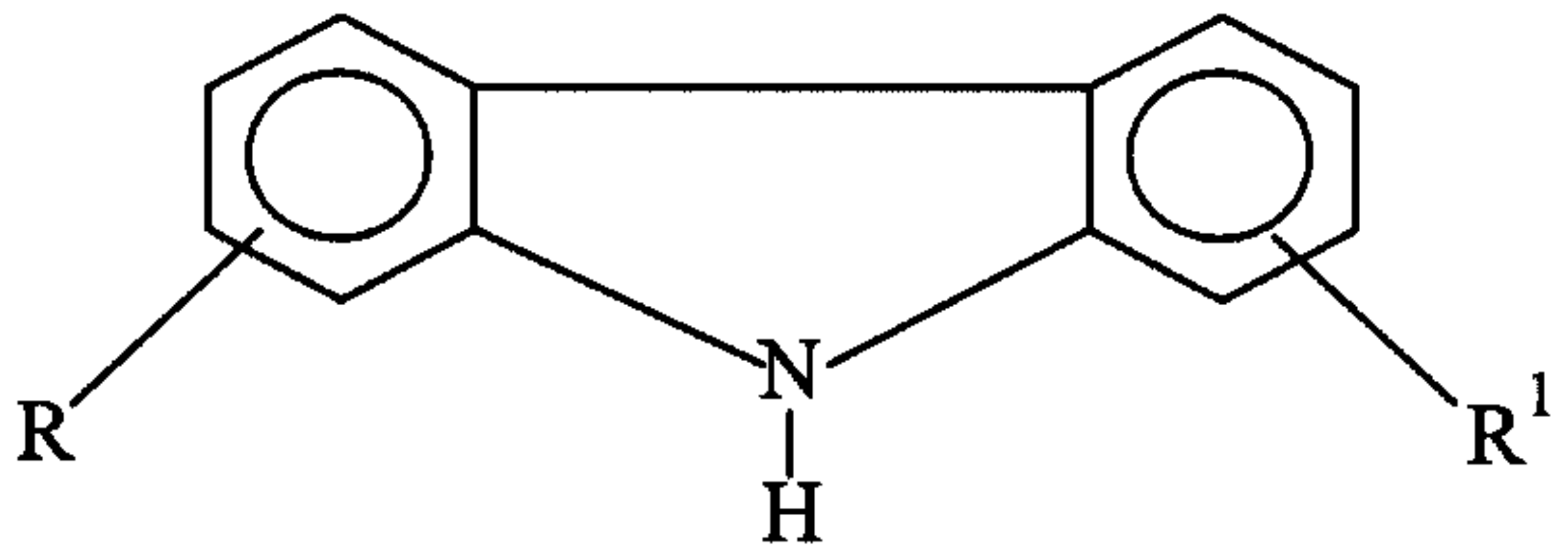


in which Ar is aromatic and R^1 is hydrogen, -NH-aryl, -NH-arylkyl, a branched or straight chain radical having from 4 to 24 carbon atoms that can be alkyl, alkenyl, alkoxyl, aralkyl, alkaryl, hydroxyalkyl or aminoalkyl,

R^2 in NH_2, $CH_2-(CH_2)_n-NH_2$, -aryl-NH_2, in which n has a value from 1 to 10, and R^3 is alkyl, alkenyl, alkoxyl, aralkyl, alkaryl having from 4 to 24 carbon atoms,

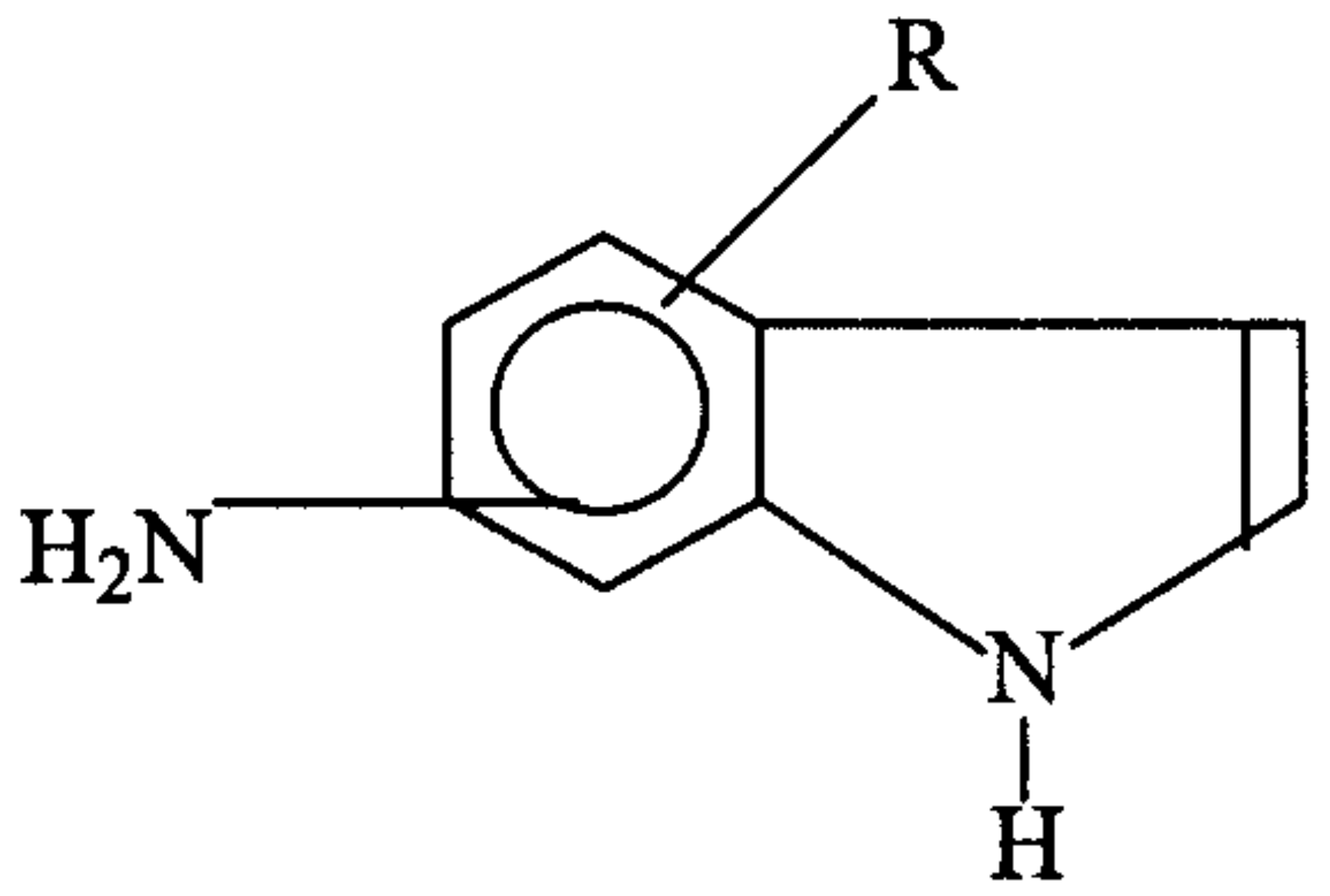
(b) an aminothiazole from the group consisting of aminothiazole, aminobenzothiazole, aminobenzothiadiazole and aminoalkylthiazole, and

(c) an aminocarbazole represented by the formula:



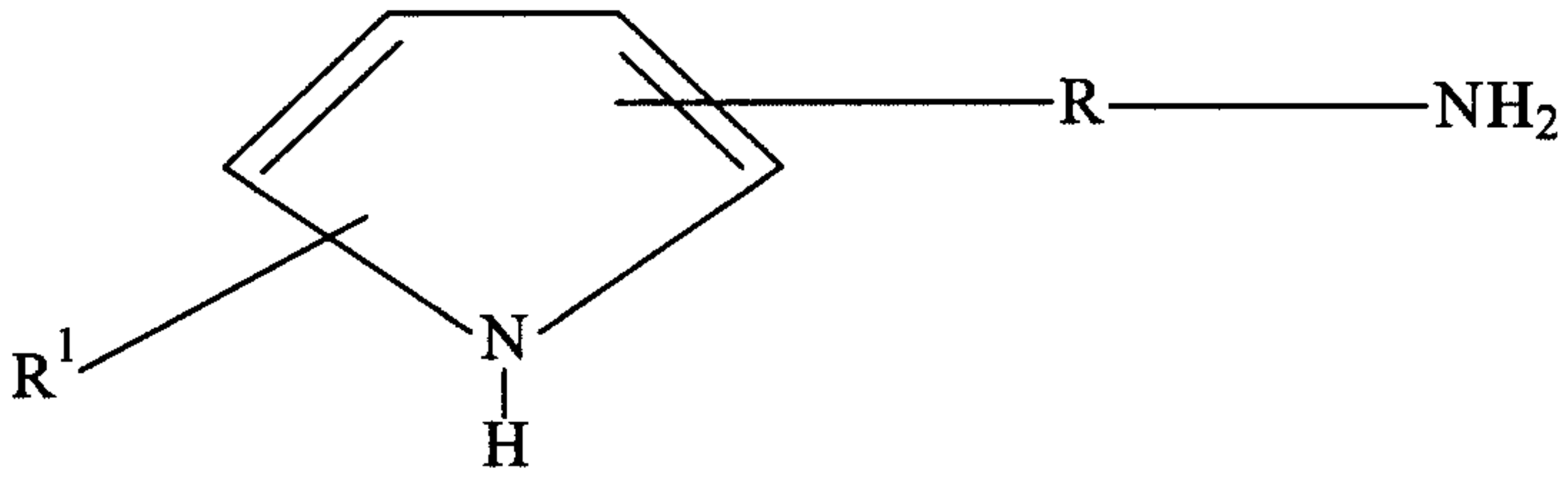
in which R and R^1 represent hydrogen or an alkyl, alkenyl, or alkoxyl radical having from 1 to 14 carbon atoms,

(d) an aminoindole represented by the formula:



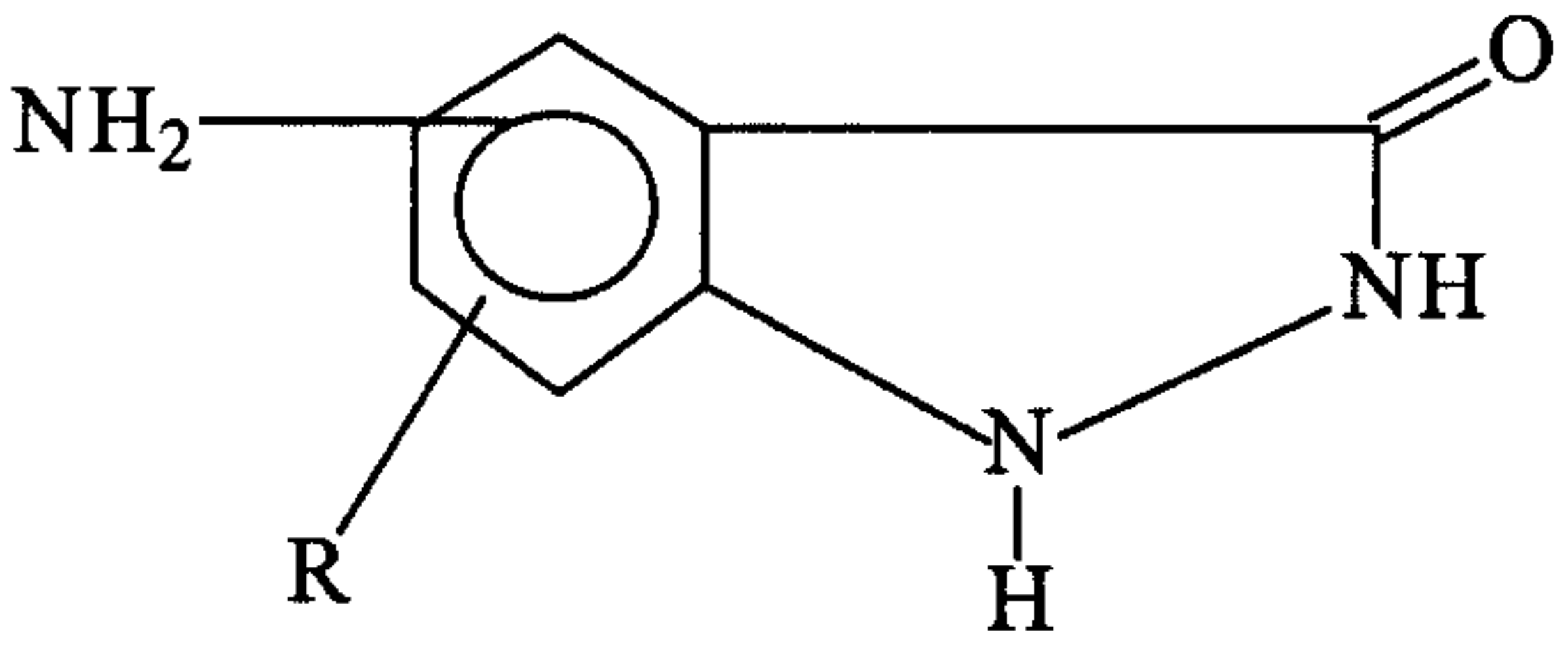
in which R represents hydrogen or an alkyl radical having from 1 to 14 carbon atoms,

(e) an aminopyrrole represented by the formula:



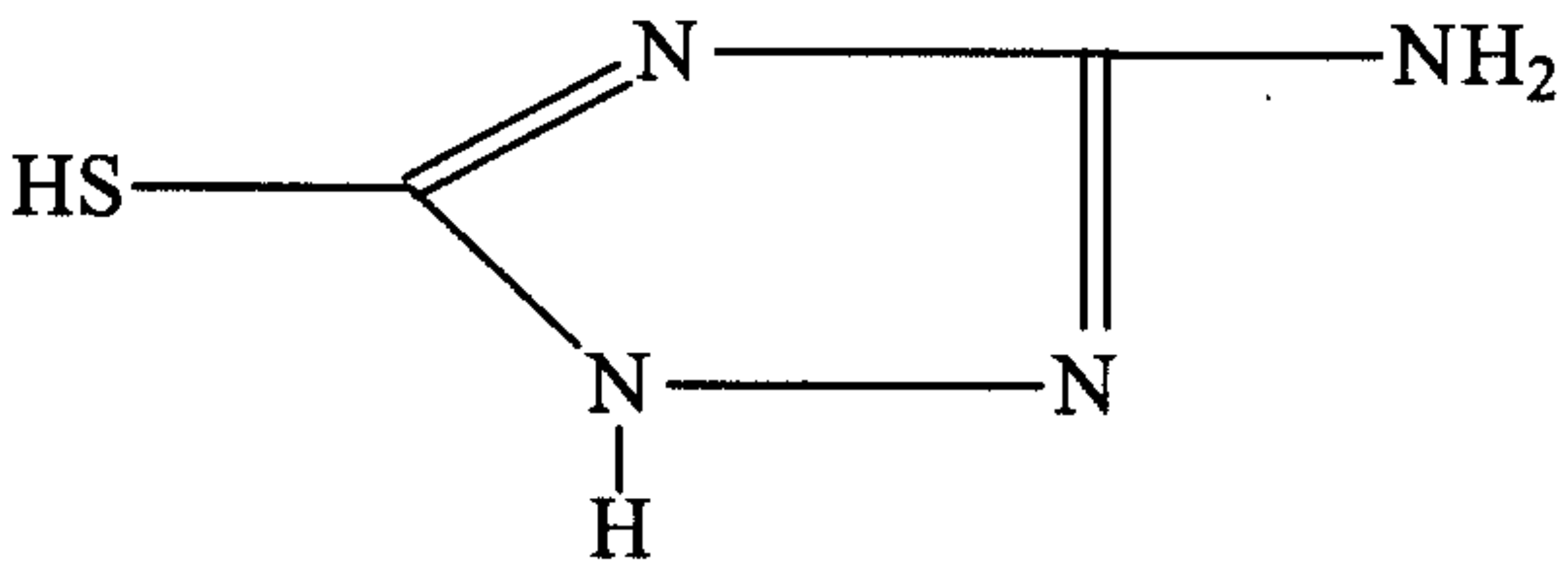
in which R is a divalent alkylene radical having 2-6 carbon atoms and R^1 is by hydrogen or an alkyl radical having from 1 to 14 carbon atoms,

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

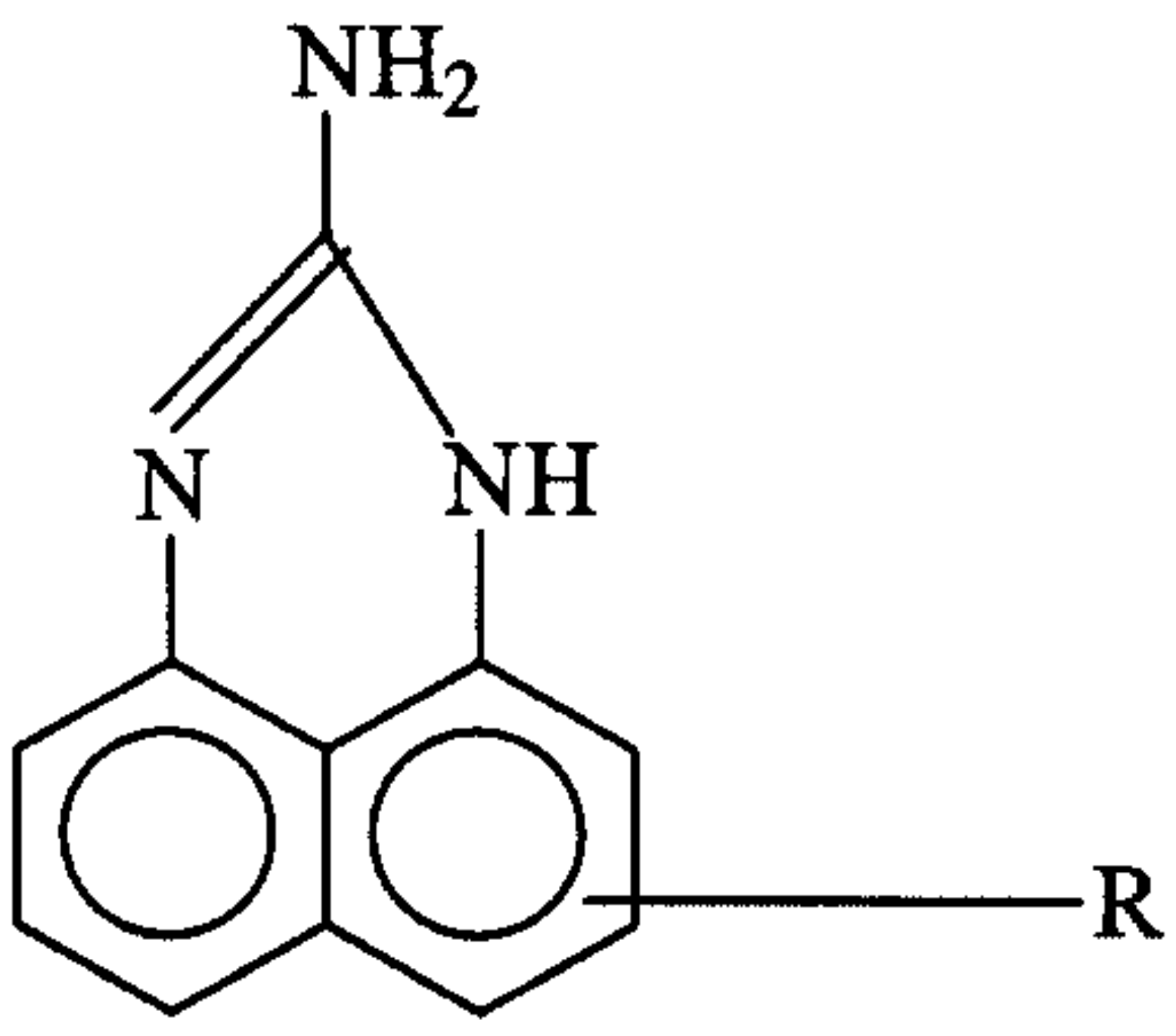


in which R is hydrogen or an alkyl radical having from 1 to 14 carbon atoms,

(g) an aminomercaptotriazole represented by the formula:



(h) an aminoperimidine represented by the formula:



in which R represents hydrogen or an alkyl or alkoxyl 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, N-phenyl-1,2-phenylenediamine, N-naphthyl-phenylenediamine, N-phenyl-naphthalenediamine and N'-aminopropyl-N-phenylphenylenediamine.

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°C 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

Preparation of the dispersant-antioxidant from ethylene-propylene copolymer (15,000 Number Avg. MW) grafted with 2.5% maleic anhydride

A 62.5 weight percent mixture of ethylene-propylene copolymer grafted with 2.5 weight percent maleic anhydride in oil (600 g) was charged into a 3000 mL 4-neck kettle along with 100 P Pale oil (600 g). The kettle was equipped with a mechanical stirrer, thermometer, thermocouple, and nitrogen inlet and heated to 160°C. Next, N-phenyl-p-phenylenediamine (28 g, 0.153 moles) was added along with Surfonic N-40* (30 g, 0.076 moles). The reaction temperature was maintained at 160°C

* Trade-mark

for 3 hours. The product (an approximately 30% concentrate) analyzed as follows: %N = 0.37 (0.34 calc.), Total Acid Number (TAN) = 1.90, and Total Base Number (TBN) = 6.08.

EXAMPLE II

The mechanical/thermal shearing preparation of dispersant-antioxidant from ethylene-propylene copolymer utilizing an extruder

The ethylene-propylene copolymer (100,000 Number Avg. MW) was chopped and processed through an extruder in a molten state at a temperature near 400°C. Just prior to entering the extruder screw, maleic anhydride was mixed with the molten polymer and the polymer exiting from the die face of the extruder was grafted with 2.2% maleic anhydride. The ethylene-propylene copolymer grafted with 2.2 weight percent maleic anhydride (1000 g) was dissolved in 100 P Pale oil (1691 g) in a 4000 mL 4-neck kettle at 160°C. The kettle was equipped with a mechanical stirrer, thermometer, thermocouple, and nitrogen inlet. Next, N-phenyl-p-phenylenediamine (44.5 g, 0.242 moles) was added along with Surfonic N-60* (80 g). The reaction temperature was maintained at 160°C for 6 hours. The product (an approximately 37% concentrate) analyzed as follows: %N = 0.37 (0.24 calc.), Total Base Number (TBN) = 7.4, and Kinetic Viscosity (100°C) = 23,008 cst.

EXAMPLE III

The synthesis of dispersant-antioxidant from ethylene-propylene copolymer (15,000 Number Avg. MW) grafted with 2.5% maleic anhydride

A 62.5 weight percent mixture of ethylene-propylene copolymer grafted with 2.5 weight percent maleic anhydride in oil (400 g) was charged into a 3000 mL 4-neck kettle along with

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* Trade-mark

100 P Pale oil (400 g). The kettle was equipped with a mechanical stirrer, thermometer, thermocouple, and nitrogen inlet and heated to 160°C. Next alkylated N-phenyl-p-phenylenediamine (20 g, 0.066 moles) was added along with Surfonic N-40* (20 g). The reaction temperature was maintained at 160°C for 6 hours. The product (an approximately 31% concentrate) analyzed as follows: %N = 0.30 (0.17 calc.), Total Acid Number (TAN) = 4.0, Total Base Number (TBN) = 0.1, and Kinetic Viscosity (100°C) = 712 cst.

EXAMPLE IV

The synthesis of dispersant-antioxidant from ethylene-propylene copolymer (15,000 Number Avg. MW) grafted with 2.5% maleic anhydride using a mixture of amines

A 62.5 weight percent mixture of ethylene-propylene copolymer grafted with 2.5 weight percent maleic anhydride in oil (1200 g) was charged into a 4000 mL 4-neck kettle along with 100 P Pale oil (1200 g). The kettle was equipped with a mechanical stirrer, thermometer, thermocouple, and nitrogen inlet and heated to 160°C. Next, N-phenyl-p-phenylenediamine (17.3 g, 0.094 moles) and N,N-dimethylaminopropylamine (9.6 g, 0.094 moles) was added along with Surfonic N-40* (60 g). The reaction temperature was maintained at 160°C for 6 hours. The product (an approximately 31% concentrate) analyzed as follows: %N = 0.31 (0.42 calc.), Total Acid Number (TAN) = 2.1, Total Base Number (TBN) = 3.1, and Kinetic Viscosity (100°C) = 1382 cst.

EXAMPLE V (Comparison Example)

The synthesis of dispersant-antioxidant from ethylene-propylene copolymer (15,000 Number Avg. MW) grafted with 1.0% maleic anhydride

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* Trade-mark

A 62.5 weight percent mixture of ethylene-propylene copolymer grafted with 1.0 weight percent maleic anhydride in oil (1431.5 g) was charged into a 4000 mL 4-neck kettle along with 100 P Pale oil (957.4 g). The kettle was equipped with a mechanical stirrer, thermometer, thermocouple, and nitrogen inlet and heated to 160°C. Next, N-phenyl-p-phenylenediamine (18.4 g, 0.099 moles) was added along with Surfonic N-40* (71.5 g). The reaction temperature was maintained at 160°C for 6 hours. The product (an approximately 37% concentrate) analyzed as follows: %N = 0.12 (0.11 calc.), Total Acid Number (TAN) = 1.8, Total Base Number (TBN) = 0.2, and Kinetic Viscosity (100°C) = 1486 cst.

EXAMPLE VI

The mechanical/thermal shearing preparation of dispersant-antioxidant from ethylene-propylene copolymer utilizing a simple reaction vessel

The ethylene-propylene copolymer (43,000 Number Avg. MW) grafted with 2.5% maleic anhydride (592 g) was dissolved in 100 P Pale oil (2370 g) at 160°C. This was done in a 3000 mL 4-neck kettle which was equipped with a mechanical stirrer, thermometer, thermocouple, and nitrogen inlet. The temperature was slowly raised to 325°C and held for 1 hour. Next, N-phenyl-p-phenylenediamine (29.0 g, 0.163 moles) was added along with Surfonic N-60* (47 g). The reaction temperature was maintained at 160°C for 6 hours. The product (an approximately 25% concentrate) analyzed as follows: %N = 0.29 (0.27 calc.), Total Acid Number (TAN) = 0.6, Total Base Number (TBN) = 2.5, and Kinetic Viscosity (100°C) = 501 cst.

EXAMPLES VII TO XIII

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* Trade-mark

Derivatized graft polymers are prepared employing the polymer and procedure described in Example I employing the following amino-aromatic polymines:

Example VII: Aminothiazole
Example VIII: Aminocarbazole
Example IX: Aminoindole
Example X: Aminoperimidine
Example XI: Aminopyrrole
Example XII: Aminomercaptotriazole
Example XIII: N-phenyl-1,3-phenylenediamine

The prescribed graft and derivatized polymer of the invention are useful as additives for lubricating oils. Specifically, they provide dispersancy, and anti-oxidant properties in single grade 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 about 0.1 to 30 weight percent. A concentration range for the additive ranging from about 0.5 to 15 weight percent based on the total weight of the oil composition is preferred with a still more preferred concentration range being from about 1 to 7.5 weight percent.

Oil concentrates of the additives may contain from about 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 60 mole percent ethylene, 40 mole percent propylene having an average molecular weight of about 15,000. 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 Weight
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	4-10

Analyses

Viscosity Kin 40C CS	30.4
Viscosity Kin 100C CS	5.33
Pour Point, F.	+10
Ash Sulfated, % D874	0.88
Phosphorus, % X-Ray	0.12
Sulfur, % X-Ray Total	0.32
Zinc, % X-Ray	0.13

Oil had a sp. Gr. 60/60°F of 0.858-0.868; Vis 100°F 123-133; Pour Point 0°F. Oil B had a sp. Gr. 60/60°F of 0.871-0.887; Vis. 100°F 325-350; Pour Point +10°F. Zinc salt is a salt of mixed alcohols-isopropanol and P_2S_5 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 C_{20}-C_{40} monoalkylbenzene sulfuric acid (MV 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 tested 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 concentrations of 4 and 6.5 weight percent polymer solution. The numerical value of the test results decreases with an increase in effectiveness.

TABLE II
BENCH VC DISPERSANCY TEST

Additive	Results[1] 4% Conc.	 6.5% Conc.
Example I	25	21
Premium Grade Commercial Motor Oil	46	20
Example II	18	21
Example III	21	13
Example IV	25	19
Example V	26	22
Reference[2]	34	18

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1. All Bench Sludge Test results are the average of duplicate runs.
2. Alkenylsuccinimide dispersant.

The anti-oxidant properties of the novel reaction product in a lubricating oil was determined in the Bench Oxidation Test. In this test, the additive reaction product is blended into solvent neutral oil (S.U.S. at 100°F of 130) at a nitrogen concentration of 0.10 weight percent. 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.

TABLE III

BENCH OXIDATION TEST

Additive	Result[1]
Example I	2.9
Reference[2]	20.7

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[1] A number below 7 indicates the anti-oxidant properties of the blend.

[2] Alkenylsuccinimide dispersant.

The test results above 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 a known commercial motor oil composition.

ASTM Sequence VE Test

The ASTM Sequence VE test is used to evaluate the performance of engine oils in protecting engine parts from sludge and varnish deposits and valve train wear due to low temperature "stop and go" operation. The test uses a Ford 2.3 L four-cylinder Ranger truck engine. The engine is cycled through three test stages, requiring four hours to complete, for 288 hours or 72 cycles. The Sequence VE engine test results shown in Table 2 were run in a 30W single grade formulation.

TABLE IV

Sequence VE Engine Test Results

Dispersant	AS[1]	AV	PSV	% ORC	% OSC
Reference[2,3] (2.4% Active)	7.1	4.3	6.8	39.8	33.6
Example I (2.0% Active)	9.5	5.0	7.3	5.0	0.0
Example IV (2.0% Active)	9.5	4.8	7.1	23.0	0.0
Example I (1.3% Active) mixed with Alkenyl Succinimide Dispersant (1.1% Active)	9.4	6.5	6.9	0.0	0.0
Limits	9.0 min	5.0 min	6.5 min	15.0 max	20.0 max

[1] AS, AV, PSV, ORC, and OSC denote: average sludge, average varnish, piston skirt varnish, oil ring clogging, and oil screen clogging, respectively.

[2] average of seven runs

[3] Alkenyl Succinimide Dispersant

The MWM-B engine test is used to evaluate the performance of diesel engine oils. The test uses a one cylinder engine that runs for 50 hours. The piston is rated for cleanliness utilizing a merit system. The rating scale goes from 0 to 80, with 80 being a perfectly clean piston. The engine test results below show that a 2.5% graft level provides superior diesel engine performance as compared to a 1% graft level for the same MW polymer. The dispersants were evaluated in a SAE 40W single grade formulation at 6.5 weight percent:

DISPERSANT	MWM-B ENGINE TEST RESULT
Example I (2.5% Maleic Anhydride)	60 Merits
Example V (1% Maleic Anhydride)	54 Merits

Haze in a lubriating oil composition represents a serious quality problem. The prescribed additives of the invention which were prepared by a variety of processes were tested for their effect on haze in oils in a Hazitron* instrument. The Hazitron is an instrument which is used to give a relative indication of light scattering caused by haze. The method is based on measurements of transmitted light by the sample placed in two positions of the sample compartment. A cuvette filled with the sample is placed in the extreme right side of the sample compartment, adjacent to the measuring photocell and the instrument is balanced with the numbered dial set on "0". The cuvette is then shifted to the extreme left side of the sample compartment and the instrument is rebalanced using the numbered dial. The reading on the numbered dial minus the cuvette correction number gives the Hazitron number. The higher the number the hazier the sample. The measurements were done on the polymer concentrates diluted to 10 volume percent in SNO-150. The results below show that samples prepared from mechanical/thermal shearing have much better clarity than samples produced from solution polymerization.

The dispersant-anti-oxidant additive of the instant invention derives its effectiveness as an anti-oxidant from the use of the specific N-arylphenylenediamine reactants described. It is contemplated, however, that valuable economies may be achieved when the prescribed reaction products of the invention are used in combination with other reaction products prepared from different amines. More specifically, grafted copolymers having the prescribed molecular weight range and prescribed

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graft level may be reacted with an amine having in its structure one primary amine group and either a tertiary amine group or a highly hindered secondary amine group. Examples of such amines include aminopropylmorpholine, aminoethylmorpholine, N',N'-dimethylaminopropylamine, N',N'-dimethylethylamine, N-methylaminopropylpiperzine.

The following table illustrates the use of such mixed reaction products.

DISPERSANT	HAZITRON NUMBER
Example I (Solution Polymerization)	80
Example II (Mechanical/Thermal Shearing)	19
Example IV (Solution Polymerization w/Mixed Amine System)	44
Example VI (Mechanical/Thermal Shearing)	25

The foregoing test results demonstrate that the antioxidant moiety can be mixed in all proportions with other polyamines on the polymer backbone and produce a useful product. This technique was used to lower the Hazitron Number of a product derived from solution polymerization from 80 to 44 without loss of engine performance.

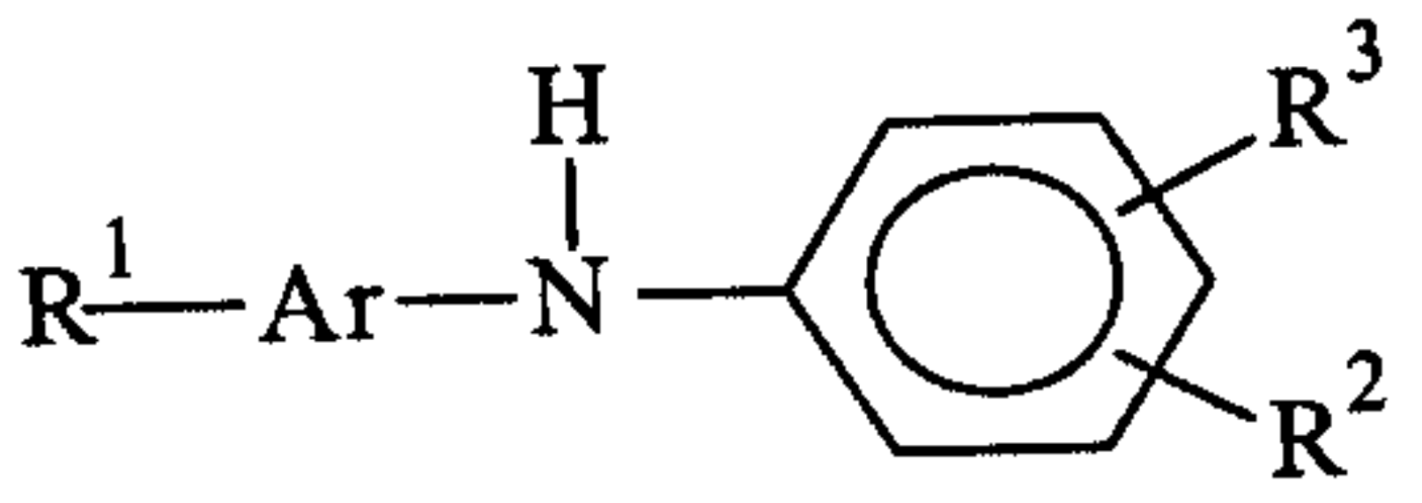
CLAIMS:

1. An additive composition prepared by a process comprising the steps of:

(A) providing a polymer intermediate having at least about 1.5 weight percent of a carboxylic acid acylating function grafted thereon, the polymer intermediate being based on a polymer substrate backbone which is (i) a copolymer of from about 15 to about 80 mole percent of ethylene and from about 85 to about 20 mole percent of at least one C_3-C_{10} alpha-monoolefin or (ii) a terpolymer of from about 15 to about 80 mole percent of ethylene, from about 85 to 20 mole percent of at least one C_3-C_{10} alpha-monoolefin and from about 0.1 to about 10 mole percent of a non-conjugated diene or triene and which has an average molecular weight ranging from about 1,000 to 40,000 and onto which at least one ethylenically unsaturated carboxylic acid material has been grafted, and

(B) then reacting the polymer intermediate with an amino-aromatic polyamine compound selected from the group consisting of:

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



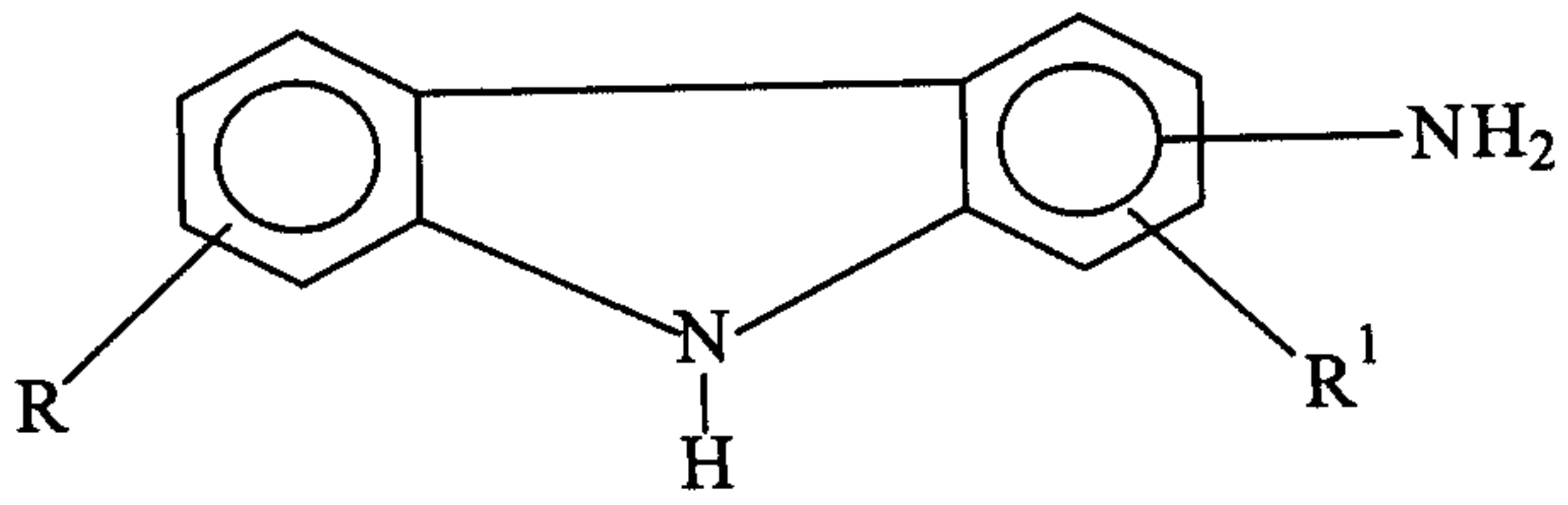
(I)

in which Ar is an aromatic hydrocarbon radical, R^1 is hydrogen, -NH-aryl, -NH-arylalkyl, a branched or straight chain radical having from 4 to 24 carbon atoms that is an alkyl, alkenyl, alkoxy, aralkyl, alkaryl, hydroxyalkyl or aminoalkyl radical, R^2 is $-NH_2$, $-CH_2-(CH_2)_n-NH_2$, $-CH_2$-aryl-NH_2 in which n has a value from 1 to 10, and

R^3 is hydrogen or an alkyl, alkenyl, alkoxy, aralkyl or alkaryl radical each having 4 to 24 carbon atoms;

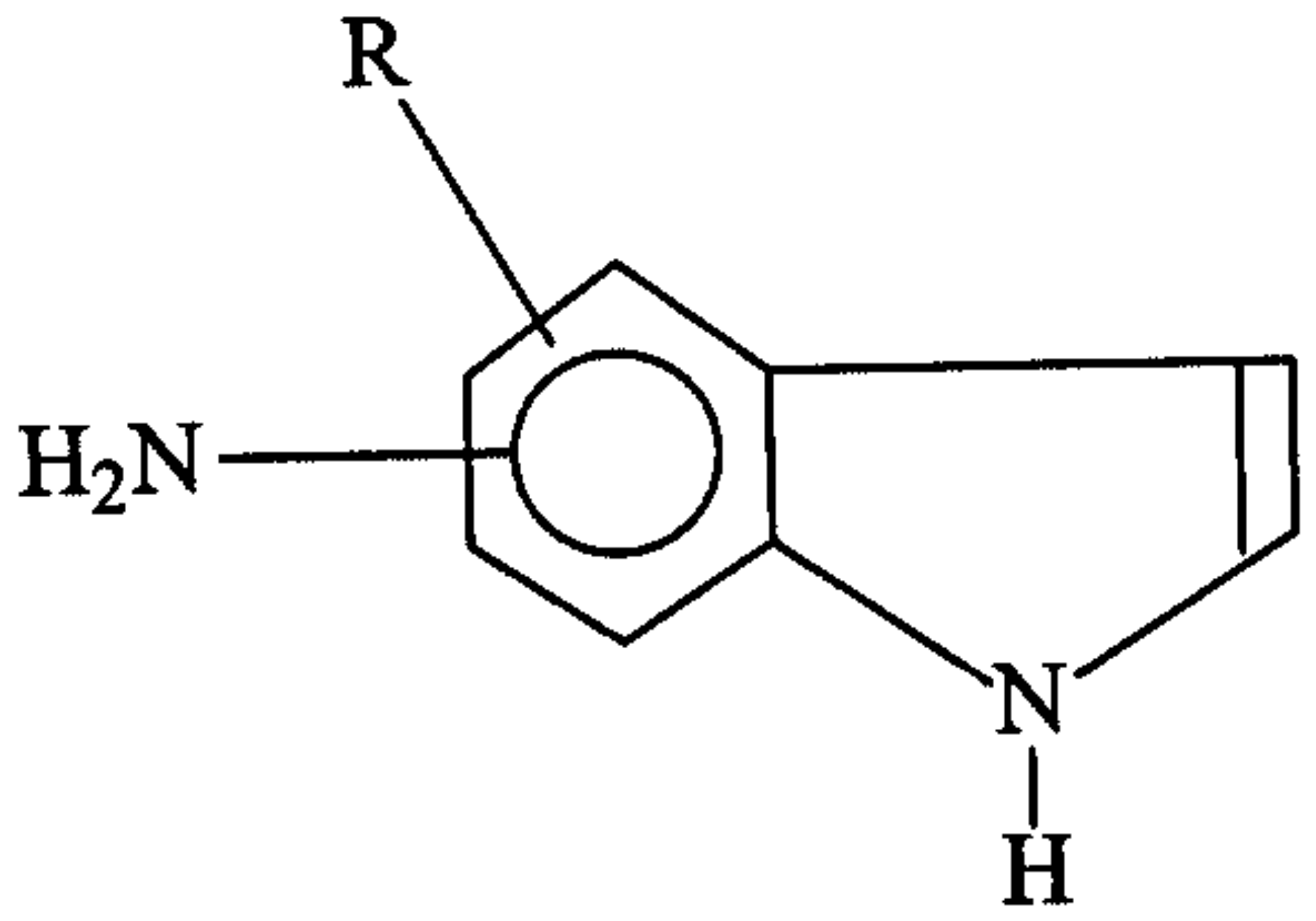
(b) an aminothiazole selected from the group consisting of aminothiazole, aminobenzothiazole, aminobenzothiadiazole and aminoalkylthiazole;

(c) an aminocarbazole represented by the formula



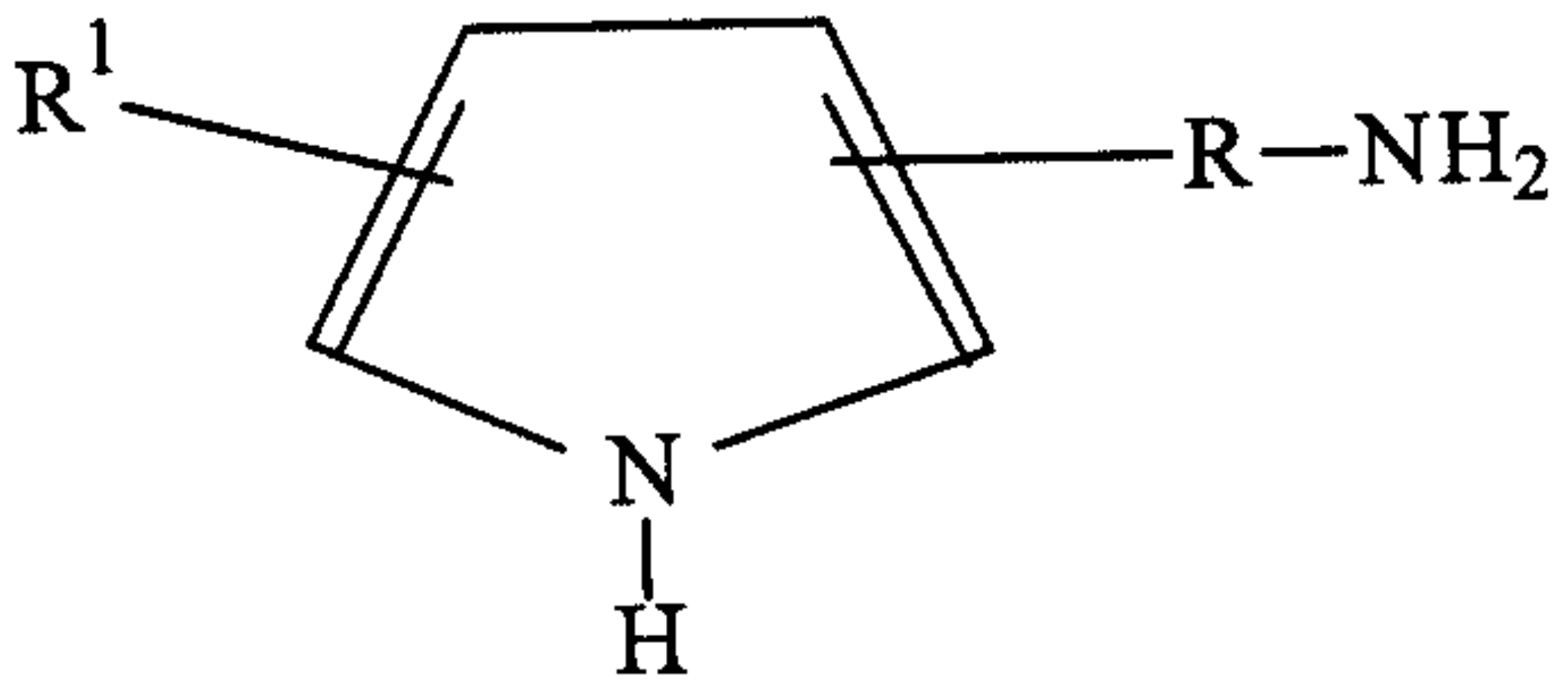
in which R and R^1 represent hydrogen or an alkyl or alkenyl radical having from 1 to 14 carbon atoms;

(d) an aminoindole represented by the formula:



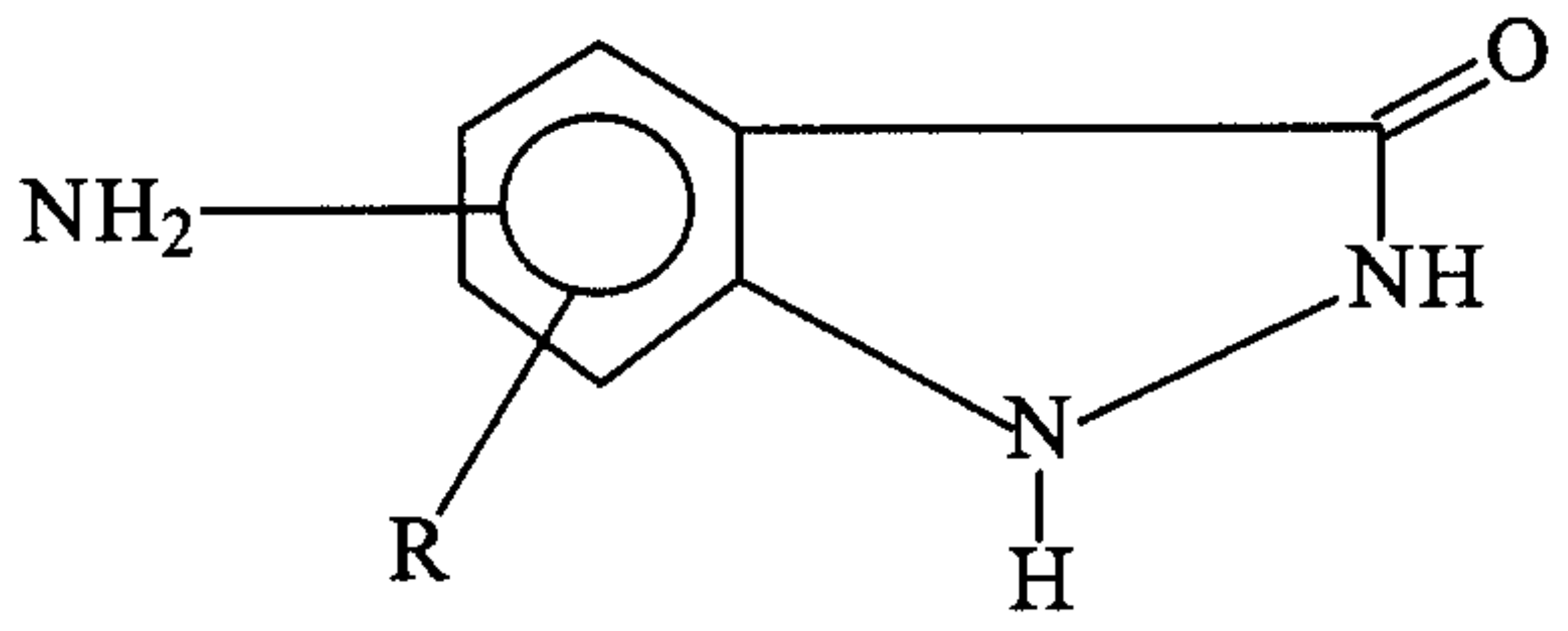
in which R represents hydrogen or an alkyl radical having from 1 to 14 carbon atoms;

(e) an aminopyrrole represented by the formula:



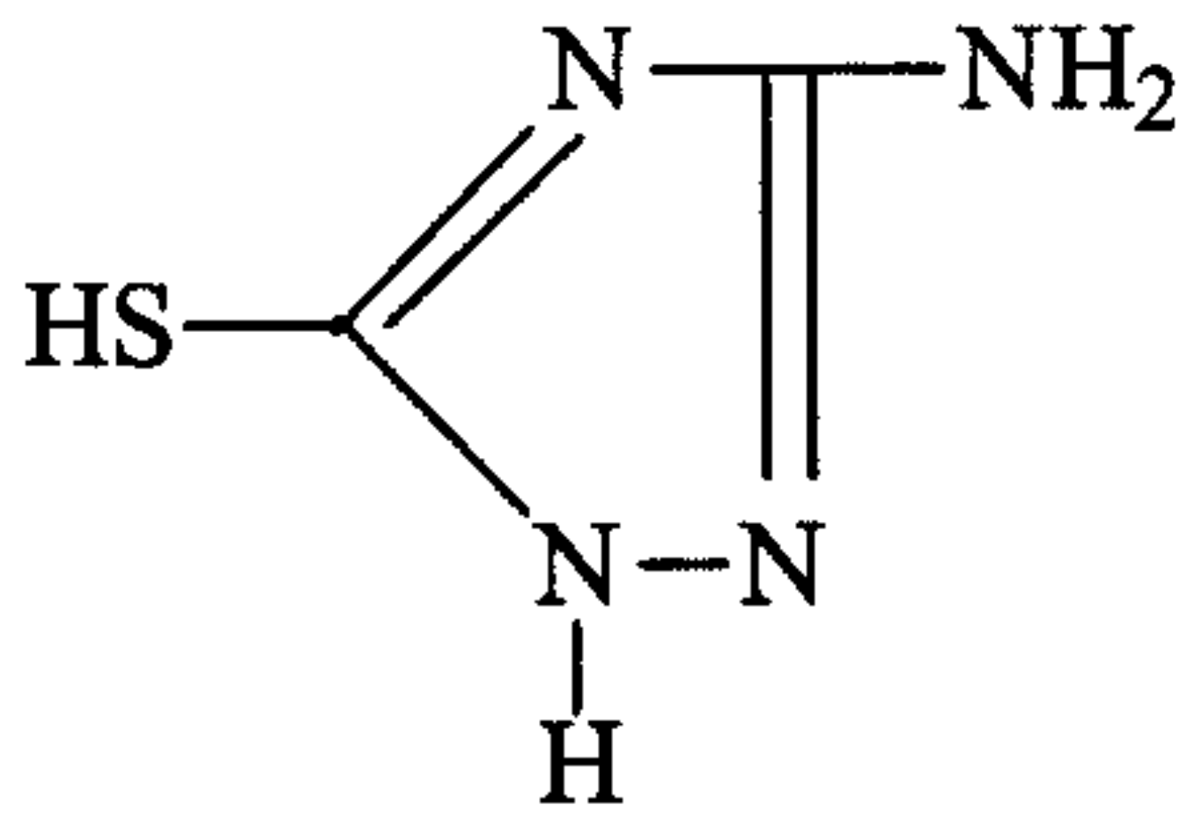
in which R is a divalent alkylene radical having 2 - 6 carbon atoms and R^1 is hydrogen or an alkyl radical having from 1 to 14 carbon atoms;

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



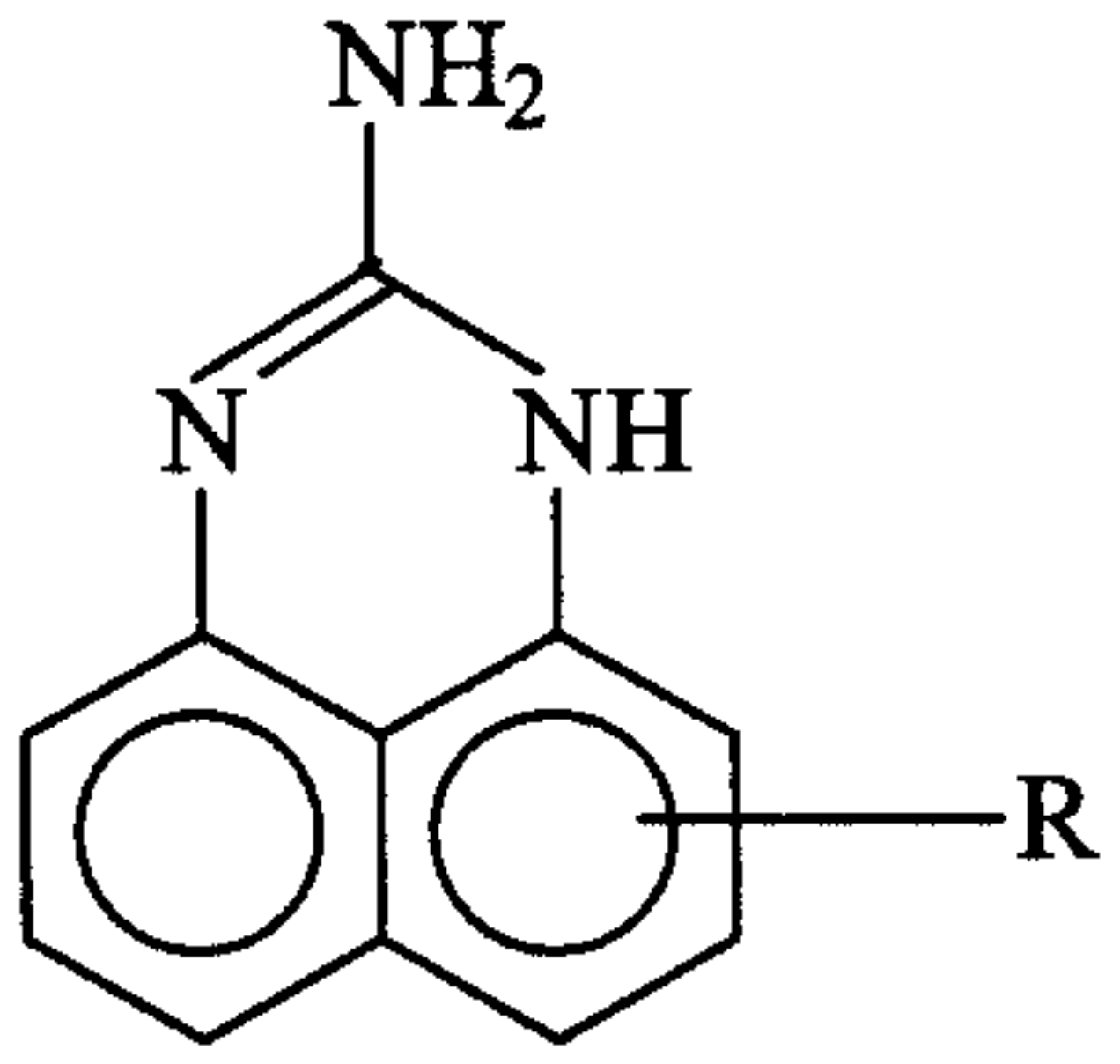
in which R is hydrogen or an alkyl radical having from 1 to 14 carbon atoms;

(g) an aminomercaptotriazole represented by the formula:



and

(h) an aminoperimidine represented by the formula:



in which R represents hydrogen or an alkyl, alkenyl, or alkoxy radical having from 1 to 8 carbon atoms.

2. A composition according to Claim 1 in which the polymer intermediate has a number average molecular weight from about 5,000 to 20,000.

3. A composition according to Claim 1, in which the polymer intermediate has a number-average molecular weight from about 8,000 to 17,000.

4. A composition according to any one of Claims 1 to 3, in which the polymer substrate is a copolymer of from about 25 to 75 mole percent ethylene and from about 75 to 25 mole percent of a C_3 to C_8 alpha-monoolefin.

5. A composition according to any one of Claims 1 to 3, in which the polymer substrate is a copolymer of from about 25 to 55 mole percent ethylene and from about 45 to 75 mole percent of propylene.

6. A composition according to any one of Claims 1 to 4, in which the polymer substrate is a terpolymer of from about 25 to 75 mole percent ethylene, from about 75 to about 25 mole percent of a C_3 to C_8 alpha-monoolefin and from about 0.1 to 10 mole percent of a non-conjugated diene or triene.

7. A composition according to any one of Claims 1 to 6, in which the ethylenically unsaturated carboxylic acid material is maleic anhydride.

8. A composition according to any one of Claims 1 to 6, in which the ethylenically unsaturated carboxylic acid material is itaconic anhydride.

9. A composition according to any one of Claim 1 to 8, in which the amino-aromatic polyamine compound is the N-arylphenylenediamine of the formula (I).

10. A composition according to Claim 9, in which the N-arylphenylene diamine is N-phenylphenylenediamine.

11. A composition according to Claim 9, in which the N-arylphenylene diamine is N-phenyl-p-phenylenediamine.

12. A composition according to Claim 9, in which the N-arylphenylene diamine is N-phenyl-1,3-phenylenediamine.

13. A composition according to any one of Claims 1 to 9, in which the amino-aromatic polyamine compound is the aminothiazole(b).

14. A composition according to any one of Claims 1 to 13, in which the polymer intermediate has from 2 to 5 weight percent of the grafted carboxylic acid acylating function.

15. A composition according to any one of Claims 1 to 14, in which the polymer intermediate has from about 2.25 to 3 weight percent of the grafted carboxylic acid acylating function.

16. A process for producing the additive composition as defined in any one of Claims 1 to 14, which comprises:

(A) obtaining the polymer intermediate having a number-average molecular weight of from about 1,000 to about 40,000 and having at least 1.5 weight percent of a carboxylic acid acylating function grafted thereon, by:

(1) providing a polymer substrate which is (i) a copolymer of from about 15 to about 80 mole percent of ethylene and from about 85 to about 20 mole percent of at least one C_3-C_{10} alpha-monoolefin or (ii) a terpolymer of from about 15 to about 80 mole percent of ethylene, from about 85 to about 20 mole percent of at least one C_3-C_{10} alpha-monoolefin and from about 0.1 to about 10 mole percent of a non-conjugated diene or triene and which has a number-average molecular weight of above about 75,000,

(2) grafting the polymer substrate with an ethylenically unsaturated carboxylic acid material, and

(3) degrading the polymer substrate by a mechanical or thermal shearing process to reduce the number-average molecular weight to from about 5,000 to 40,000,

where the steps (2) and (3) may be conducted simultaneously or sequentially in any order; and

(B) then reacting the polymer intermediate with the amino-aromatic polyamine compound.

17. A process according to Claim 16, in which the grafting step (2), of the polymer substrate with the ethylenically unsaturated carboxylic acid material is effected using a mechanical shearing process.

18. A process according to Claim 16, in which the grafting step (2) of the polymer substrate with the ethylenically unsaturated carboxylic acid material is effected using a thermal or melt grafting process at a temperature which is from about 150 to about 400°C and at which the polymer substrate is molten.

19. A process according to Claim 18, in which the thermal or melt grafting process is effected in an extruder.

20. A process according to any one of Claims 16 to 19, in which the grafting step (2) and the degrading step (3) are effected simultaneously.

21. A process according to any one of Claims 16 to 20, in which the polymer substrate has a number-average molecular weight of 100,000 to 300,000.

22. A composition which is a mixture of the additive composition of any one of Claims 1 to 15 or the additive composition prepared by the process of any one of Claims 16 to 21 and a reaction product of a grafted polymer and an amine other than the amino-aromatic polyamine having in its structure one primary amine group and either a tertiary or a highly hindered secondary amine group, wherein the grafted polymer has the same characteristics as the polymer intermediate.

23. A composition according to Claim 22, wherein the amine other than the amino-aromatic polyamine is selected from the group consisting of aminopropylmorpholine, aminoethylmorpholine, and N-methylaminopropylpiperazine.

24. A lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor amount effective to impart dispersancy and anti-oxidant properties to the oil of the additive composition of any one of Claims 1 to 15 or the additive composition produced by the process of any one of Claims 16 to 21.

25. A lubricating oil composition according to Claim 24, which contains from about 0.1 to about 30 weight percent of the additive composition.

26. A lubricating oil composition according to Claim 24, which contains from about 0.5 to about 15 weight percent of the additive composition.

27. A lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor amount effective to impart dispersancy and anti-oxidant properties to the oil of the composition of Claim 22 or 23.

28. A single grade lubricating oil composition comprising an oil of lubricating viscosity and from about 0.5 to 15 weight percent of the additive of Claim 11.

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