

Description

The invention relates to a process for the preparation of an oil composition comprising polymeric viscosity index (V.I.) improvers - dispersant additives for use in synthetic and petroleum oils, particularly lubricating oils. These additives comprise a hydrocarbon polymer, for example a copolymer of ethylene with one or more C₃ to C₂₈ alpha-olefins, preferably propylene, or a hydrogenated copolymer of styrene and butadiene or isoprene, etc., which have been grafted either with nitrogen-containing monomers, such as vinyl pyridine, vinyl pyrrolidone, aminomethacrylate, etc. or which have been grafted with an acid moiety, e.g. maleic anhydride, preferably followed by reaction with an amine, which will usually be a polyamine. The invention relates also to the use of the products of these processes in oil, particularly lubricating and fuel compositions. The processes include the direct reaction of either the nitrogen-containing monomer or the unsaturated acid compound with the hydrocarbon polymer per se, preferably in the solid state; that is, in the absence of solvent or diluent, wherein the grafting is carried out using a free radical generator, e.g. a peroxide or azo initiator, together with a chain stopping agent, e.g. such as a mercaptan or hydroxyl amine in order to hinder cross-linking and occurrence of oil insolubility.

Prior Disclosures

Ethylene copolymers, particularly ethylene-propylene copolymers, are in widespread use as viscosity index (V.I.) improving additives for oil compositions, particularly lubricating oil compositions. A substantial body of prior art exists directed towards further reacting these ethylene V.I. improvers to form a multi-functional V.I. improver. This is a material useful as a V.I. -dispersant oil additive so as to improve not only the V.I. properties of the oil but to also impart dispersancy so as to suspend sludge that may form during the operation or use of the lubricant and to inhibit varnish deposition in engines. Various patents teach grafting ethylene copolymers with maleic anhydride, followed by reaction with an amine, either in an oil as a solvent or in a synthetic solvent such as dichlorobenzene, such as the processes disclosed in U.S. Patents 4,137,185, 4,144,181 and 4,069,794. Similarly, prior patents, such as U.S. 4,092,255, 4,146,489 and 4,170,561, were directed towards grafting the ethylene copolymer directly with a nitrogen compound, such as vinyl pyridines and vinyl pyrrolidones, usually in a chemical solvent, such as dichlorobenzene, or in an oil as a solvent.

The use of solvents for carrying out these reactions involves the expense of subsequently removing the solvent and redissolving the additive in oil to form an oil concentrate, which is the usual way that such additives are marketed. In addition, many of such solvents, such as chlorinated hydrocarbons which do not chain transfer, are expensive and toxic. The idea of carrying out the reaction directly in an oil eliminated the necessity of removing the solvent and gave an economic benefit. However, subsequent problems have arisen using the oil technique since the grafting reaction results in not only the ethylene copolymer being grafted but also various compounds of the oil reacting to form unwanted materials. These unwanted grafted oil materials are not only ineffective as V.I. improvers or as dispersants, but in many cases may cause haze due to the formation of insoluble materials, and are detrimental to engine performance. In addition, the reaction with the oil molecules uses up valuable reactants.

A third approach was to carry out the formation of the desired V.I.-dispersant additive in the absence of any substantial amount of solvent, either oil or synthetic solvent, at least in carrying out the grafting reaction. This approach has been suggested by various prior art patents, such as U.S. 4,068,056; 4,068,057 and 4,068,058, wherein amines are directly grafted upon an ethylene-propylene copolymer by mastication or by an extruder, either under a nitrogen atmosphere as in 4,068,057 or in the presence of oxygen as in 4,068,058 and 4,068,056.

U.S. 3,862,265 has a broad disclosure of extruder-grafting a wide range of polymers including ethylene-propylene elastomers with various monomers, including maleic anhydride. U.K. Patent 857,797 teaches grafting polymers by mastication using peroxide and in the presence of oxygen or air. U.K. 1,119,629 grafts maleic anhydride onto synthetic rubber in an extruder using inhibitors to control cross-linking. U.K. 832,193 has an extensive disclosure wherein various monomers were grafted by mastication upon various polymers using various techniques. The use of chain stopping agents or chain transfer agents have been suggested to inhibit cross-linking, as in U.S. Patent 4,160,072; published Japanese Patent Application JA 53-110453 (Publication No. 55-36274) 1980, and in Japanese Patent Publication No. 46-35370 (1971).

The use of non-ethylene hydrocarbon polymers to form V.I.-dispersant additives is also known in the art, such as those of U.S. Patents 3,903,003; 4,077,893 and U.S. 4,141,847.

The present invention is a further improvement in forming useful oil soluble additives, wherein the grafting is carried out with the hydrocarbon polymer, preferably a polyolefin in the form of a solid rubber in

the substantial absence of any chemical solvent or lubricating oil. This avoids the need to remove the chemical solvent and it avoids the grafting of the oil molecules during the course of the reaction. The present invention preferably utilizes free radical generators, such as peroxides, in order to speed up the graft reaction. However, simply grafting the hydrocarbon polymer, e.g. ethylene copolymer per se, either in an extruder or a masticator with peroxide has been found to result in cross-linking the polymer with the frequent formation of insoluble gel, or insoluble gel-like portions, when it was attempted to later dissolve the grafted material in oil. On the other hand, attempting to avoid the gelling by restricting the amount of grafting was unsatisfactory since a certain amount of grafting is necessary to incorporate the desired amount of nitrogen-containing moieties to achieve the desired degree of dispersancy. Thus, the present invention differs from the above-noted prior art in utilizing both a free radical generator and a chain stopping agent in carrying out the grafting of a hydrocarbon polymer, preferably in the solid state, in the substantial absence of solvent or diluent, with an unsaturated monomer which may either be a nitrogen monomer or an unsaturated acid which can then be subsequently reacted with an amine or alcohol, eg a polyol, or amino alcohol, in a subsequent reaction to form oil soluble additives.

In accordance with the invention, there is provided a process for the preparation of an oil composition, preferably a lubricating oil composition, which comprises an oil and a viscosity index improver-dispersant additive, the process comprising:

- (i) grafting a hydrocarbon polymer of C_2 to C_{28} olefin, said polymer having a number average molecular weight in the range of from 5,000 to 500,000 with an unsaturated material selected from the group consisting of: (A) ethylenically unsaturated C_3 to C_{10} carboxylic acid having 1 to 2 carboxylic acid groups or an anhydride group, and (B) nitrogen-containing ethylenically unsaturated monomers containing 6 to 30 carbon atoms and 1 to 4 nitrogen atoms, in the presence of a free radical initiator and a chain stopping agent, the grafting reaction being carried out under an inert atmosphere and in the substantial absence of chemical solvent, so as to form a grafted material useful as a viscosity index improver-dispersant additive,
- (ii) subsequently incorporating the grafted material with an oil, preferably a lubricating oil.

DESCRIPTION OF PREFERRED EMBODIMENT

Hydrocarbon Polymer

Oil soluble hydrocarbon polymers or copolymers used in the invention generally will have a number average molecular weight ($\bar{M}_n$) of from 5000 to 500,000; preferably 10,000 to 200,000 and optimally from about 20,000 to 100,000. In general, polymers useful as V.I. improvers will be used. These V.I. improvers will generally have a narrow range of molecular weight, as determined by the ratio of weight average molecular weight ($\bar{M}_w$) to number average molecular weight ($\bar{M}_n$). Polymers having a ($\bar{M}_w/\bar{M}_n$) of less than 10, preferably less than 7, and more preferably 4 or less are most desirable. As used herein ($\bar{M}_n$) and ($\bar{M}_w$) are measured by the well known techniques of vapor phase osmometry (VPO), membrane osmometry and gel permeation chromatography. In general, polymers having a narrow range of molecular weight may be obtained by a choice of synthesis conditions such as choice of catalyst, or principal catalyst and cocatalyst combination, addition of hydrogen during the synthesis, etc. Post synthesis treatment such as extrusion at elevated temperature and under high shear through small orifices, mastication under elevated temperatures, thermal degradation, fractional precipitation from solution, etc. may also be used to obtain narrow ranges of desired molecular weights and to break down higher molecular weight polymer to different molecular weight grades for V.I. use.

Examples of suitable hydrocarbon polymer include homopolymers and copolymers of two or more monomers of C_2 to C_{28} , e.g. C_2 to C_{18} olefins, including both alpha olefins and internal olefins, which may be straight or branched, aliphatic, aromatic, alkylaromatic, cycloaliphatic, etc. Frequently they will be of ethylene with C_3 to C_{28} olefins, particularly preferred being the copolymers of ethylene and propylene, and polymers of other olefins such as propylene, butene and polyisobutylene. Also homopolymers and copolymers of C_6 and higher alpha olefins can be preferably employed.

Such hydrocarbon polymers also include olefin polymers such as atactic polypropylene, hydrogenated polymers and copolymers and terpolymers of styrene, e.g. with isoprene and/or butadiene.

The preferred polymers are prepared from ethylene and ethylenically unsaturated hydrocarbons including cyclic, alicyclic and acyclic, containing from 3 to 28 carbons, e.g. 2 to 18 carbons. These ethylene copolymers may contain from 15 to 90 wt. % ethylene, preferably 30 to 80 wt. % of ethylene and 10 to 85 wt. %, preferably 20 to 70 wt. % of one or more C_3 to C_{28} , preferably C_3 to C_{18} , more preferably C_3 to C_8 , alpha olefins. While not essential, such copolymers preferably have a degree of crystallinity of less than 25

wt. %, as determined by X-ray and differential scanning calorimetry. Copolymers of ethylene and propylene are most preferred. Other alpha-olefins suitable in place of propylene to form the copolymer, or to be used in combination with ethylene and propylene, to form a terpolymer, tetrapolymer, etc., include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, etc.; also branched chain alpha-olefins, such as 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methylpentene-1, 4,4-dimethyl-1-pentene, and 6-methylheptene-1, and mixtures thereof.

The term copolymer as used herein, unless otherwise indicated, includes terpolymers, tetrapolymers, etc., preferably of ethylene, said C₃-28 alpha-olefin and/or a non-conjugated diolefin or mixtures of such diolefins which may also be used. The amount of the non-conjugated diolefin will generally range from 0.5 to 20 mole percent, preferably 1 to 7 mole percent, based on the total amount of ethylene and alpha-olefin present.

Representative examples of non-conjugated dienes that may be used as the third monomer in the terpolymer include:

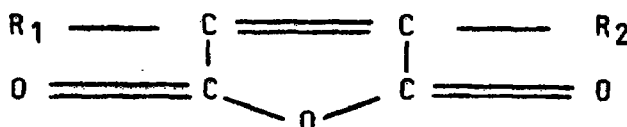
- a. Straight chain acyclic dienes such as: 1,4-hexadiene; 1,5-heptadiene; 1,6-octadiene.
- b. Branched chain acyclic dienes such as: 5-methyl-1,4-hexadiene; 3,7-dimethyl 1,6-octadiene; 3,7-dimethyl 1,7-octadiene; and the mixed isomers of dihydro-myrcene and dihydro-cymene.
- c. Single ring alicyclic dienes such as: 1,4-cyclohexadiene; 1,5-cyclooctadiene; 1,5-cyclo-dodecadiene; 4-vinylcyclohexene; 1-allyl, 4-isopropylidene cyclohexane; 3-allyl-cyclopentene; 4-allyl cyclohexene and 1-isopropenyl-4-(4-butenyl) cyclohexane.
- d. Multi-single ring alicyclic dienes such as: 4,4'-dicyclopentenyl and 4,4'-dicyclohexenyl dienes.
- e. Multi-ring alicyclic fused and bridged ring dienes such as: tetrahydroindene; methyl tetrahydroindene; dicyclopentadiene; bicyclo (2.2.1) hepta 2,5-diene; alkyl, alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as: ethyl norbornene; 5-methylene-6-methyl-2-norbornene; 5-methylene-6, 6-dimethyl-2-norbornene; 5-propenyl-2-norbornene; 5-(3-cyclopentenyl)-2-norbornene and 5-cyclohexylidene-2-norbornene; norbornadiene.

Other suitable hydrocarbon polymers may be made from styrene, and substituted styrenes, such as alkylated styrene, or halogenated styrene. The alkyl group in the alkylated styrene, which may be a substituent on the aromatic ring or on an alpha carbon atom, may contain from 1 to 20 carbons, preferably 1-6 carbon atoms. These styrene type monomers may be copolymerized with suitable conjugated diene monomers including butadiene and alkyl-substituted butadiene, etc., having from 1 to 6 carbons in the alkyl substituent. Thus, in addition to butadiene, isoprene, piperylene and 2,3-dimethylbutadiene are useful as the diene monomer. Two or more different styrene type monomers as well as two or more different conjugated diene monomers may be polymerized to form the interpolymers. Still other useful polymers are derived without styrene and only from aliphatic conjugated dienes, usually having from 4 to 6 carbon atoms most usefully, butadiene. Examples are homopolymers of 1,3-butadiene, isoprene, 1,3-pentadiene, 1,3-dimethylbutadiene, copolymers formed with at least two of these conjugated dienes and copolymers of the latter with styrene, these homopolymers and copolymers having been hydrogenated. These aforesaid polymers with considerable unsaturation are preferably fully hydrogenated to remove substantially all of the olefinic unsaturation, although, in some situations, partial hydrogenation of the aromatic-type unsaturation is effected. These interpolymers are prepared by conventional polymerization techniques involving the formation of interpolymers having a controlled type of steric arrangement of the polymerized monomers, i.e. random, block, tapered, etc. Hydrogenation of the interpolymer is effected using conventional hydrogenation processes.

Polyisobutylenes are readily obtained in a known manner as by following the procedure of U.S. Pat. No. 2,084,501 wherein the isoolefin, e.g. isobutylene, is polymerized in the presence of a suitable Friedel-Crafts catalyst, e.g. boron fluoride, aluminum chloride, etc., at temperatures substantially below 0°C. such as at -40°C. Such isobutylenes can also be copolymerized with a higher straight chained alpha-olefin of 6 to 20 carbon atoms as taught in U.S. Pat. No. 2,534,095 where said copolymer contains from about 75 to about 99% by volume of isobutylene and 1 to 25% by volume of a higher normal alpha-olefin of 6 to 20 carbon atoms. Copolymers of isobutylene with dienes such as isoprene or piperylene may also be used.

Ethylenically Unsaturated Carboxylic Acid Material

These materials which are grafted onto the hydrocarbon polymer contain 3 to 10 carbon atoms and at least one ethylenic unsaturation and one to two, preferably two, carboxylic acid groups, or an anhydride group. Maleic anhydride or a derivative thereof is preferred as it does not appear to homopolymerize appreciably but attaches onto the polymer to give two carboxylic acid functionalities. Such preferred materials have the generic formula



wherein R₁ and R₂ are hydrogen or a halogen. Suitable examples additionally include chloro-maleic anhydride, itaconic anhydride, hemi anhydride or the corresponding dicarboxylic acids, such as maleic acid or fumaric acid or their monoesters.

As taught by U.S. 4,160,739 and U.S. 4,161,452, various unsaturated comonomers may be grafted on the olefin copolymer together with the unsaturated acid component, e.g. maleic anhydride. Such graft monomer systems may comprise one or a mixture of comonomers different from the unsaturated acid component and which contain only one copolymerizable double bond and are copolymerizable with said unsaturated acid component. Typically, such comonomers do not contain free carboxylic acid groups and are esters containing α,β -ethylenic unsaturation in the acid or alcohol portion; hydrocarbons, both aliphatic and aromatic, containing α,β -ethylenic unsaturation, such as the C₄-C₁₂ alpha olefins, for example isobutylene, hexene, nonene, dodecene.; styrenes, for example styrene, α -methyl styrene, p-methyl styrene, p-sec. butyl styrene.; and vinyl monomers, for example vinyl acetate, vinyl chloride, vinyl ketones such as methyl and ethyl vinyl ketone. Comonomers containing functional groups which may cause crosslinking, gelation or other interfering reactions should be avoided, although minor amounts of such comonomers (up to about 10% by weight of the comonomer system) often can be tolerated.

Unsaturated Nitrogen Containing Monomer

Nitrogen containing unsaturated compounds are well known in forming polymers useful as oil additives. These monomers may be used for grafting onto the polymer and include, among others those having 6 to 30 carbon atoms and 1 to 4 nitrogen atoms.

Nitrogen containing acrylate and methacrylate monomers may be used such as dimethylaminoethyl methacrylate or acrylate; acrylamides and methacrylamides such as N-(1,1-dimethyl-3-oxobutyl)acrylamide, N-(1,2-dimethyl-1-ethyl-3-oxobutyl)acrylamide, N-(1,3-diphenyl-1-methyl-3-oxopropyl)acrylamide, N-(1-methyl-1-phenyl-3-oxobutyl) methacrylamide, N,N-diethylaminoethyl acrylamide, 2-hydroxyethyl acrylamide, N-dimethylaminopropyl acrylamide and methacrylamide.

N-vinylcaprolactams may be used. These include N-vinylpyrrolidone, N-vinylthiopyrrolidone, 3-methyl-1-vinylpyrrolidone, 4-methyl-1-vinylpyrrolidone, 5-methyl-1-vinylpyrrolidone, 3-ethyl-1-vinylpyrrolidone, 3-butyl-1-vinylpyrrolidone, 3,3-dimethyl-1-vinylpyrrolidone, 4,5-dimethyl-1-vinylpyrrolidone.

Vinyl pyridines may be used, such as 2-vinylpyridine, 4-vinylpyridine, and lower alkyl (C₁-C₈) substituted C-vinylpyridines, such as 2-methyl-5-vinylpyridine, 2-methyl-4-vinylpyridine, 2-vinyl-5-ethyl pyridine, 2-vinyl-6-methylpyridine.

Grafting of the Polymer

The grafting of the polymer with the carboxylic acid material or nitrogen monomer may be carried out in an extruder, a rubber mill, a Banbury mixer, Brabender mixers, and other mechanical mixing devices which can mix or knead the rubber at elevated temperatures with the other components of the reaction into a homogeneous solid rubbery mass so grafting can take place in the solid state. Combinations of equipment may also be used, such as a low temperature mixer for premixing the ingredients, following which they can be transferred to a high temperature heated mixer for grafting.

The radical grafting is preferably carried out using free radical initiators such as peroxides, hydroperoxides, and azo compounds and preferably those which have a boiling point greater than about 100°C. and which decompose thermally within the grafting temperature range to provide said free radicals. Representative of these free-radical initiators are azobutyro-nitrile, di-lauroyl peroxide, 2,5-di-methyl-hex-3-yne-2, 5 bis-tertiary-butyl peroxide (sold as Lupersol® 130) or its hexane analogue, di-tertiary butyl peroxide and dicumyl peroxide. The initiator is generally used at a level of between 0.005% and 1%, e.g. 0.05 to 0.5%, based on the total weight of the ethylene copolymer, and temperatures of 120 to 250°C.

The ethylenically unsaturated nitrogen monomer or carboxylic acid material, preferably maleic anhydride, will be generally used in an amount ranging from 0.1 to 10%, preferably 0.5 to 5.0%, based on weight of the initial ethylene copolymer. The aforesaid carboxylic acid or nitrogen monomer material and

free radical initiator are generally used in a weight percent ratio range of 1.0:1 to 30:1, preferably 4.0:1 to 12:1.

The chain stopping agent is preferably an aliphatic mercaptan having 4 to 24 carbon atoms, such as t-butyl mercaptan, n-butyl mercaptan, octyl mercaptan, n-dodecyl mercaptan, t-dodecyl mercaptan. The tertiary mercaptans and diethyl hydroxyl amine are particularly effective and are the most preferred. Other chain stopping agents may be used, for example, cumene, alcohols, phenols, etc. The chain stopper will be generally used in an amount of 0.05 to 10 wt. %, e.g. 0.1 to 5 wt. %, based on the weight of the ethylene copolymer.

The initiator grafting is preferably carried out at 120°-250°C., preferably 150°-220°C. An inert atmosphere, such as that obtained by nitrogen blanketing can be used. While the grafting can be carried out in the presence of air, the yield of the desired graft polymer is generally thereby decreased as compared to grafting under an inert atmosphere substantially free of oxygen. The total time will usually range from about 0.005 to 12 hours. If carried out in an extruder, the total time will be relatively short, e.g. 0.005 to 0.2 hours. In a masticator usually from 0.5 to 6 hours, more preferably 0.5 to 3 hours, total time will be required. The graft reaction will be usually carried out to at least approximately 4 times, preferably at least about 6 times, the half-life of the free-radical initiator at the reaction temperature employed, e.g. with 2,5-dimethyl hex-3-yne-2,5-bis(t-butyl peroxide) 2 hours at 160°C. and one hour at 170°C.

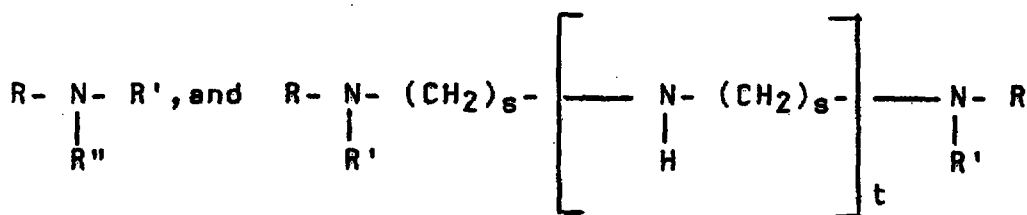
In the grafting process, usually the polymer rubber is first heated to 100-160°C. and below the grafting temperature to facilitate mixing with the other ingredients, such as the unsaturated graft material, e.g. maleic anhydride, chain stopper and initiator, all of which are added with mixing to form a homogeneous mixture. The chain stopper is preferably added before the initiator. The reaction mixture can then be further heated to grafting temperatures, preferably in the range of 170 to 240°C. Grafting temperature is the temperature where the initiator breaks down to form free radicals and cause substantial grafting to take place. When the reaction is complete, the excess monomer material may be eliminated by an inert gas purge, e.g. nitrogen sparging. Continuous or periodic addition of the graft material to the reactor can be utilized along with an appropriate portion of initiator and chain stopper during the course of the reaction.

In some cases the grafting can take place in several stages by mixing the reactants together below the grafting temperature; heating to a higher temperature to graft; cooling below grafting temperature; adding and mixing more unsaturated material, initiator and chain stopper; heating again to the grafting temperature to graft the added material, etc. In still other cases, it may be desirable to heat the polymer to grafting temperature and add the chain stopper, the unsaturated acid or nitrogen monomer and the initiator all while at grafting temperatures. Alternatively, the chain stopper can be added to the polymer below grafting temperature, and the initiator and unsaturated acid or nitrogen monomer can be added at grafting temperatures.

After the grafting is complete, diluent oil, such as mineral lubricating oil, may be mixed into the grafted ethylene copolymer to form a concentrate. This dilution can be carried out in a masticator used for the grafting, or dilution can be carried out in a separate heating and mixing vessel. The oil solution can be the final additive product if the grafting used a N-containing monomer. On the other hand, if unsaturated acid or anhydride, such as maleic anhydride, was grafted on the polymer, then a further reaction with an amine or hydroxy component is carried out to form a V.I.-dispersant additive. This will usually be carried out using the diluted grafted polymer in a separate reaction vessel from that used for grafting.

The Amine Component

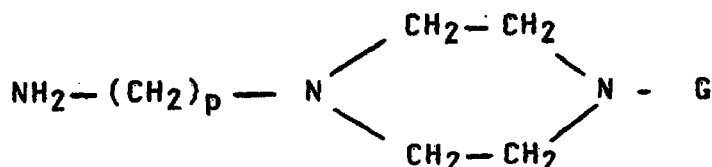
Useful amine compounds for neutralization of the acid, e.g. maleic anhydride, grafted polymer include mono- and polyamines of from 2 to 60, e.g. 3 to 20, total carbon atoms and from 1 to 12, e.g., 2 to 7 nitrogen atoms in the molecule. These amines may be hydrocarbyl amines or may be hydrocarbyl amines including other groups, e.g., hydroxy groups, alkoxy groups, amide groups, imidazoline groups, and the like. Hydroxy amines with 1 to 6 hydroxy groups, preferably 1 to 3 hydroxy groups are particularly useful. Preferred amines are aliphatic saturated amines, including those of the general formulas:



wherein R, R' and R'' are independently selected from the group consisting of hydrogen; C₁ to C₂₅ straight or branched chain alkyl radicals; C₁ to C₁₂ alkoxy C₂ to C₆ alkylene radicals; C₂ to C₁₂ hydroxy amino alkylene radicals; and C₁ to C₁₂ alkylamino C₂ to C₆ alkylene radicals; s is a number of from 2 to 6, preferably 2 to 4; and t is a number of from 0 to 10, preferably 2 to 6.

Examples of suitable amine compounds include: 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; polypropylene amines such as 1,2-propylene diamine; di-(1,2-propylene)triamine; di-(1,3-propylene)triamine; N,N-dimethyl-1,3-diaminopropane; N,N-di-(2-aminoethyl)ethylene diamine; N,N-di-(2-hydroxyethyl)-1,3-propylene diamine; 3-dodecyloxypropylamine; N-dodecyl-1,3-propane diamine; tris-hydroxymethylaminomethane (THAM); diisopropanol amine; diethanol amine; triethanol amine; mono-, di-, and tri-tallow amines; N-amino alkyl morpholines where the alkyl is 0 to 5 carbons such as N-(2-aminoethyl) morpholine; N-(3-aminopropyl)morpholine; substituted pyridines such as 2-amino pyridine; 2-methylamino pyridine; and 3-methylamino pyridine; 2-(2-aminoethyl) pyridine; 2-(4-aminoethyl) pyridine; and other amines including 2-amino pyrimidine; 2-amino benzothiazole; 2-aminothiazole; 2-amino-2-thiazoline; methyl-1-phenyl hydrazine; isopropyl ethylene diamine; and para-morpholino aniline.

Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines, and N-aminoalkyl piperazines of the general formula:



wherein G is independently selected from the group consisting of hydrogen and omega-aminoalkylene radicals of from 1 to 3 carbon atoms, and p is an integer of from 0 to 4, e.g. 1 to 4. Non-limiting examples of such amines include 2-pentadecyl imidazoline; N-(2-aminoethyl) piperazine; etc.

Commercial mixtures of amine compounds may advantageously be used. For example, one process for preparing alkylene amines involves the reaction of an alkylene dihalide (such as ethylene dichloride or propylene dichloride) with ammonia, which results in a complex mixture of alkylene amines wherein pairs of nitrogens are joined by alkylene groups, forming such compounds as diethylene triamine, triethylenetetramine, tetraethylene pentamine, pentaethylene hexamine, and isomeric piperazines. Low cost poly(ethyleneamines) compounds having a composition approximating tetraethylene pentamine are available commercially under the trade name "Polyamine H" and "Polyamine 400" (PA-400).

Especially preferred are amines having a single primary amine group, with any other amine groups present being tertiary amine groups. This minimizes cross-linking and becomes particularly important when the polymer has a relatively high degree of acidity, e.g. above 0.1 meq./g. of polymer. Mixtures comprising about 70 wt. % or more of amines having only a single primary or secondary group may be used with small amounts of amines having two or more primary or secondary amine groups. Acidities below 0.1 meq./g. polymer are less sensitive to cross-linking and amines with 2 or more reactive groups, i.e. either primary or secondary amine groups, or both primary and secondary amine groups, or a primary amine group and an alcohol group, may be used.

The Alcohol Component

The V.I.-ashless dispersants may be esters derived from the aforesaid polymer grafted with carboxylic acid or anhydride and from hydroxy compounds such as monohydric and polyhydric alcohols or aromatic compounds such as phenols and naphthols etc. The polyhydric alcohols are the most preferred hydroxy compound and preferably contain from 2 to 10 hydroxy radicals, for example, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, and other alkylene glycols in which the alkylene radical contains from 2 to 8 carbon atoms. Other useful polyhydric alcohols include glycerol, monooleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, dipentaerythritol, etc.

The ester dispersant may also be derived from unsaturated alcohols such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexane-3-ol, and oleyl alcohol. Still other classes of the alcohols capable of yielding the esters of this invention comprise the ether-alcohols and amino-alcohols including, for example, the oxy-alkylene, oxy-arylene-, amino-alkylene-, and amino-arylene-substituted alcohols having one or more oxy-alkylene, amino-alkylene, amino-arylene or oxy-arylene radicals. They are exemplified by Cellosolve®, Carbitol®, and N,N,N',N'-tetrahydroxy-trimethylene di-amine. For the most part, the ether-alcohols having up to about 150 oxy-alkylene radicals in which the alkylene radical contains from 1 to 8 carbon atoms are preferred.

Especially preferred are monoalcohols when the acidity is above 0.1 meq./g. of polymer, while polyols may be used at acidities below 0.1 meq./g. of polymer. Preferred V.I.-ester dispersant additives are diesters of succinic anhydride moieties formed by grafting ethylene copolymer with maleic anhydride.

Reaction of Grafted Polymer with Amine or Alcohol Components

The polymer, grafted with acidic moieties, preferably in solution generally equal to about 5 to 30 wt. %, preferably 10 to 20 wt. % polymer, can be readily reacted with amines or alcohols by heating at a temperature of from 100°C. to 250°C., preferably from 120 to 230°C., for from 0.5 to 10 hours, usually 1 to 6 hours. The heating is preferably carried out to favor formation of imides, and amides in the case of amine components, or esters in the case of alcohol components. Reaction ratios can vary considerably, depending upon the reactants, amounts of excess, type of bonds formed, etc.

Compositions

A minor amount, e.g. 0.001 up to 50 wt. %, preferably 0.005 to 25 wt. %, based on the weight of the total composition, of the oil-soluble graft polymers produced in accordance with this invention can be incorporated into a major amount of an oleaginous material, such as a lubricating oil or hydrocarbon fuel, depending upon whether one is forming finished products or additive concentrates. When used in lubricating oil compositions, e.g., automotive or diesel crankcase lubricating oil, the final grafted polymer V.I.-dispersant concentrations are usually within the range of 0.01 to 10 wt. %, e.g., 0.1 to 6.0 wt. %, preferably 0.25 to 3.0 wt. %, of the total composition. The lubricating oils to which the products of this invention can be added include not only hydrocarbon oil derived from petroleum, but also include synthetic lubricating oils such as esters of dicarboxylic acids; complex esters made by esterification of monocarboxylic acids, polyglycols, dicarboxylic acids and alcohols; polyolefin oils, etc.

The V.I.-dispersant graft polymers of the invention may be utilized in a concentrate form, e.g., from 5 wt.% up to 50 wt. %, preferably 7 to 25 wt. %, in oil, e.g., mineral lubricating oil, for ease of handling.

The above oil compositions may contain other conventional additives, such as dyes, pour point depressants, antiwear agents, antioxidants, other viscosity-index improvers, dispersants, etc.

The following examples, wherein all parts are parts by weight, which include preferred embodiments, further illustrate the present invention without constituting a limitation in the scope thereof.

EXAMPLE 1

1816 g. of ethylene-propylene solid rubber were added through a hatch in the top of a 9.5 liter laboratory masticator, which was then closed, and heated to 140°C. while mixing under a nitrogen stream for about 45 minutes. This mixing caused the rubber to band, that is form a sticky cohesive mass around the masticator mixer blades. Then, 65 g. of tert. dodecyl mercaptan as chain stopper were added over about 5 minutes, followed by the addition of 62 g. of maleic anhydride over another 5 minutes. Next, 7.3 g. of Lupersol® 130 dissolved in 7.3 g. of polyisobutylene of 500 M_n mol. wt. for ease of handling were added over another 5 minutes. Mixing under nitrogen at 140°C. continued during all of said additions.

The temperature was then raised over about 15 minutes to 190°C., where the Lupersol rapidly breaks

down and the major proportion of the grafting takes place. The masticator contents were then heat soaked at 190°C. for 20 minutes, followed by nitrogen stripping at 1.25 hours at 190°C. to remove unreacted maleic anhydride and other volatiles. Then 4540 g. of S100NLP (Solvent Neutral lubricating oil of 100 SUS viscosity at 37.8°C, low pour) were added over a period of 1.75 hours at 190°C. The temperature was then dropped to 160°C. for 30 minutes, after which the masticator was drained to give the Product of Example 1. All of the preceding was carried out while mixing under a nitrogen atmosphere. The Product of Example 1 was a clear, viscous oil solution of the maleic anhydride grafted rubber. The grafted polymer in this Product analyzed 0.149 milliequivalents of acid per g. of polymer, which indicated that about 43% of the maleic anhydride charged to the masticator had reacted.

The laboratory masticator used above was a Beken Duplex Mixer manufactured by the Bramley Machinery Corp., Edgewater, N.J. It had a 9.51 (2-1/2 gal.) reactor space heated by a Dow Therm containing outer jacket. The mixing blades were mounted on two oppositely rotating shafts. One shaft was rotated at 26 rpm while the other rotated at 52 rpm. Dropping funnels were used to feed the mercaptan, maleic anhydride, and Lupersol 130 solution into the reactor. The reactor was fitted with a nitrogen inlet and an exit vent.

The ethylene-propylene copolymer used above was a V.I. improver for lubricating oil and consisted of about 43 wt. % ethylene and about 57 weight % propylene. It had a Thickening Efficiency (T.E.) of about 2.8 which represents a number average molecular weight of approximately 60,000. It was an amorphous copolymer with a $\bar{M}_w/\bar{M}_n$ of less than 4:1.0.

Thickening Efficiency (T.E.) is defined as the ratio of the weight percent of a polyisobutylene (sold as an oil solution by Exxon Chemical Co. as Paratone N), having a Staudinger Molecular Weight of 20,000, required to thicken a solvent-extracted neutral mineral lubricating oil, having a viscosity of 150 SUS at 37.8°C., a viscosity index of 105 and an ASTM pour point of 0°F (-17.8°C.), (Solvent 150 Neutral) to a viscosity of $12.4 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ at 98.9°C., to the weight percent of a test copolymer required to thicken the same oil to the same viscosity at the same temperature. T.E. is related to ($\bar{M}_n$) and is a convenient, useful measurement for formulation of lubricating oils of various grades.

EXAMPLE 2

200 g. of the Product of Example 1, that is the oil solution of maleic anhydride grafted ethylene-propylene copolymer were charged to a 2 liter laboratory resin kettle along with 200 g. of S100NLP mineral lubricating oil. The kettle was equipped with a heating mantle, a dropping funnel, stirrer, overhead water condenser, vacuum pump and a nitrogen inlet for maintaining a nitrogen atmosphere. The temperature was raised to 190°C. while stirring and nitrogen sparging. The temperature was maintained at 190°C. for one hour to remove any moisture or volatiles. Then 1.16 g. of 2-aminomethyl pyridine dissolved in 2.38 g. of S100NLP were added over 10 minutes, followed by continued heating at 190°C. and mixing while under nitrogen for one hour. The reaction mixture was then nitrogen stripped for one hour after which the temperature was lowered to 150°C. and 272 g. of S100NLP were added and mixed for 15 minutes, followed by nitrogen sparging for one hour. The reactor was then drained to give the Product of Example 2 which was an oil solution of the aminated maleic anhydride grafted ethylene-propylene rubber. This Product had a K.V. (Kinematic Viscosity) of $1779 \cdot 10^{-3} \text{ Pa.s}$ at 100°C. and was useful as a Viscosity Index improving - sludge dispersant additive, e.g. for lubricating oils.

The Product of Example 2 was tested for storage stability by storing in an oven at 80°C. At the end of two weeks in the oven, the K.V. at 100°C. was $1768 \cdot 10^{-3} \text{ Pa.s}$. After four weeks in the oven, the K.V. at 100°C. was $1745 \cdot 10^{-3} \text{ Pa.s}$, indicating good thermal storage stability.

EXAMPLE 3

200 grams of the Product of Example 1 were added to the 2 liter resin kettle along with 200 grams of S100NLP. The temperature was raised to 190°C. while stirring and nitrogen sparging for a period of one hour. 1.16 grams of 2-aminomethyl pyridine dissolved in 2.38 grams of S100NLP were added over a 10-minute period and reacted for one hour, while continuing the nitrogen sparging. Then the reaction mixture was nitrogen stripped for one hour at 190°C, after which the temperature was lowered to 150°C and 272 grams of S100NLP were added and mixed for 15 minutes, followed by sparging with nitrogen for another hour. The reaction mixture was then drained to give the product having a K.V. at 100°C. of $1779 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$.

EXAMPLE 4

The 2 liter resin kettle was charged with 200 grams of the Product of Example 1 and 200 grams of S100NLP. The temperature was raised to 190°C. while stirring and nitrogen sparging, which conditions were maintained for one hour, after which 0.90 grams of 2-aminopyrimidine were added and reacted for one hour under nitrogen. The reaction mixture was then stripped with nitrogen for one hour at 190°C., after which the temperature was lowered to 150°C. and 272 grams of S100NLP were added and mixed for 15 minutes. The reactor was then drained to give the product having a K.V. at 100°C. of $1774 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$

EXAMPLE 5

The 2 liter resin kettle was charged with 200 grams of the Product of Example 1 and 200 grams of S100NLP. The temperature was raised to 190°C. while nitrogen sparging and stirring for one hour, after which 1.52 grams of 2-amino benzothiazole were added and reacted for one hour. The reaction mixture was then nitrogen stripped for one hour at 190°C., after which the temperature was lowered to 150°C. and 272 grams of S100NLP were added and mixed for 15 minutes, following which the reactor was drained to give the product having a K.V. at 100°C. of $2184 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$.

EXAMPLE 6

The 2 liter resin kettle was charged with 200 grams of the Reaction Product of Example 1 and 200 grams of S100NLP. The temperature was raised to 190°C. while stirring under a nitrogen sparge and maintained for one hour. At the end of this time, 1.1 grams of 2-aminothiazole were added and reacted for one hour under the nitrogen. The reaction mixture was then nitrogen stripped for one hour at 190°C. The temperature was lowered to 150°C. and 272 grams of nitrogen sparged S100NLP were added and mixed for 15 minutes, after which the reactor was drained to give the product having a K.V. at 100°C. of $1810 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$.

EXAMPLE 7

The 2 liter resin kettle was charged with 200 grams of the Product of Example 1 and 200 grams of S100NLP. The temperature was raised to 190°C. while stirring and nitrogen sparging. Then 1.2 grams of 1-methyl-1-phenylhydrazine dissolved in 2.4 grams of S100NLP were added over a 10-minute period and reacted for one hour while lightly sparging with nitrogen. The reaction mixture was then nitrogen stripped for one hour at 190°C. The temperature was lowered to 150°C. and 272 grams of S100NLP were added and mixed for 15 minutes. The 272 grams of S100NLP had been previously nitrogen sparged for one hour before adding. The reaction mixture was then drained to give the product having a K.V. at 100°C. of $1826 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$.

EXAMPLE 8

The 2 liter resin kettle was charged with 500 grams of the Reaction Product of Example 1 and 500 grams of S100NLP. The temperature was raised to 190°C. while stirring and nitrogen sparging and held there for one hour. The temperature was then lowered to 150°C. and 5.5 grams of N-isopropylethylene diamine were added over a 15-minute period, following which the temperature was raised to 190°C. and the amine reacted for a one-hour period. The reaction mixture was then nitrogen stripped for one hour at 190°C., cooled to 150°C. where 680 grams of S100NLP were added and mixed for 15 minutes. Following this, the reactor was drained to give the product having a K.V. at 100°C. of $1438 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$.

EXAMPLE 9

The 2 liter resin kettle was charged with 200 grams of the Reaction Product of Example 1 and 200 grams of S100NLP. The temperature was raised to 190°C. and held there for one hour while stirring and nitrogen sparging. Then 1.08 grams of N-aminomorpholine were added slowly and reacted for one hour at 190°C. The reaction mixture was nitrogen stripped for one hour at 190°C., following which the temperature was lowered to 150°C. and 272 grams of S100NLP were added and mixed for 15 minutes. The reactor was then drained to give the final product having a K.V. at 100°C. of $2376 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ and a nitrogen content of 0.28 wt. %.

EXAMPLE 10

1816 grams of Nordel® 1320 was added to the reactor, that is the 9.5 liter masticator, and heated at 140°C. under nitrogen until banding occurred. Then, 20 grams of octadecyl mercaptan, 14.4 grams of N-vinyl pyrrolidone and 3.6 grams of Lupersol 130 were added to the reactor followed by heating to 170°C. for 45 minutes, while mixing under nitrogen. The reactor was then cooled to 140°C. and 10 grams of octadecyl mercaptan, 14.4 grams of N-vinyl pyrrolidone and 3.6 grams of Lupersol 130 was added to the reactor while mixing and stirring under nitrogen. The masticator, that is the reactor, was heated to 170°C. for 60 minutes under nitrogen while continuing mixing, following which 4540 grams of S100NLP were added and mixed in for about one hour. The masticator was drained to give the final product which was an oil solution of an ethylene copolymer grafted with N-vinyl pyrrolidone, which would be useful as a V.I. dispersant modifying additive in lubricating oil. The final product had a kinetic viscosity at 100°C. of $1080 \cdot 10^{-3} \text{Pa.s}$ and the grafted polymer therein had a T.E. of 1.85.

Nordel 1320 is a terpolymer of about 53 wt. %, ethylene, about 43.5 wt. % propylene and about 3.5 wt. % of 1,4-hexadiene. It has a Mooney viscosity at 100°C. of about 25 and is sold by the DuPont Company.

EXAMPLE 11

1816 grams of the ethylene-propylene rubber used in Example 1 of 2.8 T.E. were added to the 9.5 liter masticator which was then mixed for 45 minutes at 120°C. under nitrogen to form a band. Then 2 grams of Pennstop® 2697, which is diethyl hydroxyamine sold as a commercial chain stopping agent, were added over a period of about five minutes. Then 30 grams of N-vinyl pyrrolidone was added over a 5-minute period. This was followed by the addition of 2 grams of Di-CUP-R (dicumyl peroxide), dissolved in 4 grams of polyisobutylene of 500 molecular weight over a 5-minute period. The temperature of the reaction mass was then raised to 160°C. and maintained for a soak period of 30 minutes. 30 grams of N-vinyl pyrrolidone was added at the 160°C. temperature followed by 2 grams of Di-CUP-R® dissolved in 4 grams of the 500 molecular weight polyisobutylene, followed by a heat soaking period, while mixing, of 60 minutes at 160°C. After this, the temperature was raised to 175°C. and 10 lbs. of S100NLP were added, followed by nitrogen stripping for 1-1/4 hours. The reactor was then drained to give the final product having the following characteristics:

K.V. at 100°C. = $1467 \cdot 10^{-6} \text{m}^2 \text{s}^{-1}$

Nephelometer Haze = 71 (At a reading of about 75 haze will become visible to the naked eye.);

Nitrogen Content of 0.30 wt. % based on the grafted polymer; and a

T.E. for the grafted polymer of 2.60.

EXAMPLE 12

1816 grams of the ethylene-propylene rubber of Example 1 was added to the 9.5 liter masticator reactor and mixed for 45 minutes at 120°C. under nitrogen. Then 2 grams of Pennstop 2697 were added and mixed in. 30 grams of N-vinyl pyrrolidone were added over a 5-minute period followed by the addition of 2 grams of Di-CUP-R dissolved in 4 grams of polyisobutylene of 500 molecular weight (PIB 500) over a period of 5 minutes. The temperature was then raised to 160°C. and maintained for a soak period of 30 minutes. Following this 1 gram of Pennstop 2697 was added over 5 minutes, 30 grams of N-vinyl pyrrolidone was added over 5 minutes, followed by the addition of 2 grams of Di-CUP-R, in 4 grams of PIB 500 in 5 minutes, later followed by 5 minutes of mixing. Then 2 grams of Di-CUP-R in 4 grams of PIB 500 was added, followed by 5 minutes of mixing. Then 2 grams of Pennstop 2697 was added followed by mixing for 5 minutes. Next, 30 grams of N-vinyl pyrrolidone was added followed by mixing for 5 minutes, followed by the addition of 2 grams of Di-CUP-R dissolved in 4 grams of PIB 500 followed by 5 minutes of mixing. The reactor contents were then heat soaked for 30 minutes at 160°C., followed by heating to 175°C. which temperature was maintained for 30 minutes. 10 lbs. of S100NLP were added, followed by nitrogen stripping for 1-1/4 hours. The reactor was then drained to give a product containing 0.43 wt. % nitrogen, based on the weight of grafted polymer, having a kinetic viscosity at 100°C of $969 \cdot 10^{-6} \text{m}^2 \text{s}^{-1}$, and containing a polymer having a T.E. of 1.36. At a 14.3 wt. % concentration of the reaction product in oil, the nephelometer haze reading was +111, indicating that visible haze was present.

Comparison Examples A to E

A series of examples were carried out in which the chain stopping agent was not used, which shows that the resulting material that formed resulted in the formation of gel and was not completely oil-soluble.

Comparison Example A

1.8Kg of the ethylene-propylene copolymer rubber of Example 1 having a T.E. of about 2.8 were added to the masticator. The copolymer was heated and mixed in the presence of air until its T.E. had been reduced to 2.1. The masticator was then flushed with nitrogen and 35 grams of maleic anhydride was added, while the temperature was raised to 175°C. as the material was worked in the masticator. 5 grams of Lupersol 130 were dissolved in a sufficient amount of S100NLP to make 50 milliliters (10% active ingredient) of the oil solution of the initiator. 20 milliliters of this solution were added while mixing at 175°C. under nitrogen. 30 minutes later another 10 milliliters of the solution were added. Ten minutes later another 10 milliliters of the peroxide solution were added. Ten minutes later still another 10 mil. of peroxide solution were added. This stage addition, i.e. periodic addition was done in order to obtain good dispersancy of the peroxide in the solid ethylene-propylene copolymer. The masticator contents were soaked, that is mixed, under the nitrogen blanket for another 60 minutes, after which 4540 g. of Solvent 100NLP were added and mixed, followed by draining the reactor to give the product.

Comparison Examples B to E

These were carried out in the same manner noted above except for the changes noted in the following Table.

Comparison Examples A to E are summarized in the following Table.

TABLE
Comparative Examples

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Ethylene-Propylene Copolymer, g.	1816g.	1816g.	1816g.	1816g.	1816g.
Maleic Anhydride, g.	35g.	45g.	45g.	45g.	45g.
Peroxide Addition, ml. solution	50(10%a.i.)	90(10%a.i.)	70(12%a.i.)	50(2.5%a.i.)	None
1st. addition, ml./Temp. °C.	20/175°C	30/175°C	20/150°C	20/140°C	
Time interval, min.	30 min.	30 min.	30 min.	30 min.	
2nd. addition, ml./Temp. °C.	10/175°C	20/175°C	10/150°C	10/170°C	
Time interval, min.	10 min.	10 min.	30 min.	30 min.	
3rd. Addition, ml./Temp. °C	10/175°C	20/175°C	10/150°C	10/170°C	
Time interval, min.	10 min.	10 min.	30 min.	30 min.	
4th. Addition, ml./Temp. °C	10/175°C	20/175°C	10/150°C	10/170°C	
Time interval, min.	-	-	30 min.	30 min.	
5th. Addition, ml./Temp. °C	-	-	10/150°C	-	
Time interval, min.	-	-	30 min.	-	
6th. Addition, ml./Temp. °C	-	-	10/150°C	-	

TABLE (CONTINUED)

Comparative Examples

	A	B	C	D	E
Soak Temp./Time, °C/min.	175°C/60min.	175°C/60min.	150°C/60min.	170°C/60min.	150°C/120min. 170°C/60min.
Addition of oil, g.	4540	4540	4540	4540	none
Product	Gelled	Gelled	Gelled	Gelled	No significant amount of maleic anhydride grafted.

Examples A to D of the Table show that even adding the peroxide in small increments, without the chain stopper did not prevent gelling. Example D used only 1.25 g. of actual peroxide and still gelling occurred. Example E shows that without the peroxide no substantial amount of grafting occurred.

EXAMPLE 13

Part A

45.4 Kg of the solid ethylene-propylene copolymer rubber used in Example 1 was added to a 190 liter rubber masticator in the form of five 9.1 Kg pieces. The copolymer was masticated and nitrogen stripped in the Dow-Therm heated masticator until the temperature reached 99°C. 0.45 Kg of t-dodecyl mercaptan was added through a dropping funnel over a 15 minute period, followed by the addition of 0.95 Kg of melted maleic anhydride, added through said dropping funnel. Initially, 100 ml. of the maleic anhydride was added. Then the remaining maleic anhydride was added over a 15 minute period simultaneously while adding 0.41 Kg of 0.54 Kg of an initiator solution that had been made up consisting of 0.09 Kg ditertiary butyl peroxide dissolved in a mixture consisting of 0.32 Kg of PIB 500 and 0.14 Kg of ISOPAR® M which is a hydrocarbon solvent. After this 15 minute period, then the remaining 0.13 Kg of said initiator solution were added over a five minute period. This last addition was followed by soaking and mixing for 50 minutes, followed by nitrogen stripping. Then 193 Kg S100NLP oil, which have been previously sparged with nitrogen to remove moisture and volatiles, were added to the masticator in a series of small increments, each increment being mixed into the reaction mass before the next increment. The first increment was 9.1 Kg followed by increments of 11.3 Kg, 13.6 Kg, 18.1 Kg, 22.7 Kg, 22.7 Kg, 22.7 Kg, 22.7 Kg and then the balance. The temperature was lowered to 93°C. while mixing continued. Then the masticator was drained to give the oil solution of the ethylene copolymer rubber grafted with maleic anhydride. The concentrate titrated to 0.192 meq. acid/g. of the grafted polymer.

Part B

A reactor was charged with 45.4 Kg of S150NLP mineral lubricating oil which was heated to 100°C. and nitrogen stripped. Following this, 45.4 Kg. of the oil solution of the ethylene copolymer grafted with maleic anhydride prepared in Part A were added to the reactor followed by mixing, nitrogen stripping and heating until the temperature reached 190°C. Then, 0.16 Kg of N-aminopropyl morpholine (NAPM) dissolved in 0.45 Kg of said oil was added over a 20-minute period to the reactor through an inlet line which was then followed with 0.23 Kg of said oil to flush the line. Mixing and heating continued for one hour under nitrogen after which 8.6 Kg of said oil were added, followed by vacuum stripping for one hour and then draining to give the final product, which was useful as a multi-functional V.I.-dispersant additive concentrate. This product analyzed 0.27 wt. % nitrogen based on the weight of the polymer, i.e. the aminated grafted polymer. The aminated grafted polymer had a T.E. of 2.46. The haze level of the concentrate was at a nephelometer reading of 102.

EXAMPLE 14

A lubricating oil composition was prepared by mixing 13 wt. %, based on the weight of the total composition, of the final product of Part B of Example 13; that is, the oil concentrate of the V.I. dispersant additive, about 1.4 wt. % of a nonylphenol sulfide additive as an antioxidant, 1.3 wt. % of an overbased 400 Total Base No. magnesium sulfonate additive, 1.8 wt. % of a zinc dialkyldithiophosphate additive (about 75 wt. % active ingredient), 0.25 wt. % of a pour depressant additive, and about 82.25 wt. % of a mineral lubricating oil, to form a 10W40 crankcase oil having a viscosity of about $14.5 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ at 100°C. This oil was tested in the MS-VD test and passed, having a sludge rating of 9.63; a varnish rating of 7.04; a piston skirt varnish rating of 6.77; a cam and lifter wear average of 0.013 cm and a maximum cam wear of 0.020 cm.

EXAMPLE 15

A 10W40 lubricating oil composition was prepared showing the material of the invention supplemented by other dispersants, by mixing about 12 wt. %, based on the total composition, of the final product of Part B of Example 13, 1.1 wt. % of antioxidant, 2.2% of an overbased metal sulfonate, 1.45 wt. % of a zinc dithiophosphate additive, and other dispersant/detergents along with antifoam, antifriction, and pour depressant additives, with 74.5 wt. % of lubricating oil.

Claims

1. A process for the preparation of an oil composition which comprises an oil and a viscosity index improver-dispersant additive, the process comprising:



Part A

45.4 Kg of the solid ethylene-propylene copolymer rubber used in Example 1 was added to a 190 liter rubber masticator in the form of five 9.1 Kg pieces. The copolymer was masticated and nitrogen stripped in the Dow-Therm heated masticator until the temperature reached 99°C. 0.45 Kg of t-dodecyl mercaptan was added through a dropping funnel over a 15 minute period, followed by the addition of 0.95 Kg of melted maleic anhydride, added through said dropping funnel. Initially, 100 ml. of the maleic anhydride was added. Then the remaining maleic anhydride was added over a 15 minute period simultaneously while adding 0.41 Kg of 0.54 Kg of an initiator solution that had been made up consisting of 0.09 Kg ditertiary butyl peroxide dissolved in a mixture consisting of 0.32 Kg of PIB 500 and 0.14 Kg of ISOPAR® M which is a hydrocarbon solvent. After this 15 minute period, then the remaining 0.13 Kg of said initiator solution were added over a five minute period. This last addition was followed by soaking and mixing for 50 minutes, followed by nitrogen stripping. Then 193 Kg S100NLP oil, which have been previously sparged with nitrogen to remove moisture and volatiles, were added to the masticator in a series of small increments, each increment being mixed into the reaction mass before the next increment. The first increment was 9.1 Kg followed by increments of 11.3 Kg, 13.6 Kg, 18.1 Kg, 22.7 Kg, 22.7 Kg, 22.7 Kg, 22.7 Kg and then the balance. The temperature was lowered to 93°C. while mixing continued. Then the masticator was drained to give the oil solution of the ethylene copolymer rubber grafted with maleic anhydride. The concentrate titrated to 0.192 meq. acid/g. of the grafted polymer.

Part B

A reactor was charged with 45.4 Kg of S150NLP mineral lubricating oil which was heated to 100°C. and nitrogen stripped. Following this, 45.4 Kg. of the oil solution of the ethylene copolymer grafted with maleic anhydride prepared in Part A were added to the reactor followed by mixing, nitrogen stripping and heating until the temperature reached 190°C. Then, 0.16 Kg of N-aminopropyl morpholine (NAPM) dissolved in 0.45 Kg of said oil was added over a 20-minute period to the reactor through an inlet line which was then followed with 0.23 Kg of said oil to flush the line. Mixing and heating continued for one hour under nitrogen after which 8.6 Kg of said oil were added, followed by vacuum stripping for one hour and then draining to give the final product, which was useful as a multi-functional V.I.-dispersant additive concentrate. This product analyzed 0.27 wt. % nitrogen based on the weight of the polymer, i.e. the aminated grafted polymer. The aminated grafted polymer had a T.E. of 2.46. The haze level of the concentrate was at a nephelometer reading of 102.

EXAMPLE 14

A lubricating oil composition was prepared by mixing 13 wt. %, based on the weight of the total composition, of the final product of Part B of Example 13; that is, the oil concentrate of the V.I. dispersant additive, about 1.4 wt. % of a nonylphenol sulfide additive as an antioxidant, 1.3 wt. % of an overbased 400 Total Base No. magnesium sulfonate additive, 1.8 wt. % of a zinc dialkyldithiophosphate additive (about 75 wt. % active ingredient), 0.25 wt. % of a pour depressant additive, and about 82.25 wt. % of a mineral lubricating oil, to form a 10W40 crankcase oil having a viscosity of about $14.5 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ at 100°C. This oil was tested in the MS-VD test and passed, having a sludge rating of 9.63; a varnish rating of 7.04; a piston skirt varnish rating of 6.77; a cam and lifter wear average of 0.013 cm and a maximum cam wear of 0.020 cm.

EXAMPLE 15

A 10W40 lubricating oil composition was prepared showing the material of the invention supplemented by other dispersants, by mixing about 12 wt. %, based on the total composition, of the final product of Part B of Example 13, 1.1 wt. % of antioxidant, 2.2% of an overbased metal sulfonate, 1.45 wt. % of a zinc dithiophosphate additive, and other dispersant/detergents along with antifoam, antifriction, and pour depressant additives, with 74.5 wt. % of lubricating oil.

Claims

1. A process for the preparation of an oil composition which comprises an oil and a viscosity index improver-dispersant additive, the process comprising:



(i) grafting a hydrocarbon polymer of C_2 to C_{28} olefin, said polymer having a number average molecular weight in the range of from 5,000 to 500,000 with an unsaturated material selected from the group consisting of: (A) ethylenically unsaturated C_3 to C_{10} carboxylic acid having 1 to 2 carboxylic acid groups or an anhydride group, and (B) nitrogen-containing ethylenically unsaturated monomers containing 6 to 30 carbon atoms and 1 to 4 nitrogen atoms, in the presence of a free radical initiator and a chain stopping agent, the grafting reaction being carried out under an inert atmosphere and in the substantial absence of chemical solvent, so as to form a grafted material useful as a viscosity index improver-dispersant additive,
(ii) subsequently incorporating the grafted material with an oil.

2. A process according to claim 1, wherein said hydrocarbon polymer is a hydrogenated copolymer of styrene with at least one aliphatic diene selected from the group consisting of butadiene and isoprene.
3. A process according to claim 1, wherein said hydrocarbon polymer is a copolymer of ethylene with a C_3 to C_{28} alpha olefin.
4. A process according to claim 3, wherein said hydrocarbon polymer consists essentially of ethylene and propylene.
5. A process according to claim 4, wherein said copolymer consists essentially of 30 to 80 weight % ethylene and 20 to 70 weight % propylene, and has a number average molecular weight in the range of 10,000 to 200,000.
6. A process according to claim 3, wherein said ethylene copolymer is a terpolymer of ethylene, propylene and an unsaturated diene.
7. A process according to any one of claims 1 to 6, wherein a homogeneous mixture is formed of said ethylene copolymer, unsaturated material, initiator and chain stopping agent by heating and mixing at a first temperature below the temperature at which said initiator generates substantial free radicals, and then heating and mixing at a second higher temperature at which said initiator generates substantial free radicals and a major proportion of said grafting takes place.
8. A process according to claim 7 wherein said first temperature is in the range of from 100 to 160° C and said second temperature is in the range of from 170 to 240° C.
9. A process according to claim 7 or 8 wherein said process is carried out in multiple stages, said first stage comprising forming said homogeneous mixture at said first temperature, then heating and mixing at said second temperature to effect grafting; and at least one additional stage of cooling to said first temperature, adding additional unsaturated material, initiator, and chain stopping agent at said first temperature and reheating and mixing to said second temperature to effect grafting of said additional unsaturated material.
10. A process according to claim 3 wherein said ethylene copolymer is a normally solid rubber at room temperature and mixing is carried out in a mechanical mixer which heats and kneads said rubber, unsaturated material, initiator and chain stopping agent into a homogeneous solid rubbery mass in which grafting takes place in the solid state.
11. A process according to any one of claims 1 to 10 wherein said unsaturated material is maleic anhydride.
12. A process according to any one of claims 1 to 10 wherein said nitrogen-containing monomer is selected from the group consisting of vinyl pyridines, vinyl pyrrolidones, acrylates and methacrylates.
13. A process according to any one of claims 1 to 10, wherein said unsaturated material comprises an unsaturated acid or anhydride, and said resulting grafted material is further reacted with an amine or alcohol.
14. A process according to any one of claims 1 to 11 wherein said grafted material is dissolved in a



mineral lubricating oil' and reacted with an amine having 2 to 60 carbon atoms and 1 to 12 amine groups to form an oil soluble Viscosity-Index improving - dispersant additive concentrate.

15. A process according to claim 14 wherein said amine is a polyamine having at least one primary amine group.
16. A process according to any one of claims 1 to 15, wherein the grafting reaction is carried out with the reactants mixed into a homogeneous solid mass.
17. A process according to any of claims 1 to 16 wherein said free radical initiator is a peroxide.
18. A process according to any of claims 1 to 17 wherein said chain stopping agent is a C_4 to C_{24} aliphatic mercaptan, diethyl hydroxyl amine, cumene, an alcohol or a phenol.
19. The use in a lubricating oil composition of a grafted material in accordance with any one of claims 1 to 18.
20. A lubricating oil composition in accordance with claim 19.

20 Patentansprüche

1. Verfahren zur Herstellung einer ein Öl und ein Viskositätsindexverbesserer-Dispergiermittel-Additiv umfassenden Ölzusammensetzung, bei dem
 - (i) ein Kohlenwasserstoffpolymer aus C_2 - C_{28} -Olefin mit einem durchschnittlichen zahlenmäßigen Molekulargewicht im Bereich von 5000 bis 500 000 mit einem ungesättigten Material ausgewählt aus der Gruppe bestehend aus (A) ethylenisch ungesättigter C_3 - C_{10} -Carbonsäure mit 1 bis 2 Carbonsäuregruppen oder einer Carbonsäureanhydridgruppe und (B) Stickstoff enthaltenden, ethylenisch ungesättigten Monomeren mit 6 bis 30 Kohlenstoffatomen und 1 bis 4 Stickstoffatomen in Gegenwart eines freiradikalischen Initiators und eines kettenstoppenden Mittels gepropft wird, wobei die Pfropfreaktion in einer inerten Atmosphäre und im wesentlichen in Abwesenheit von chemischem Lösungsmittel durchgeführt wird, um ein gepropftes Material zu bilden, das als Viskositätsindexverbesserer-Dispergiermittel-Additiv brauchbar ist, und
 - (ii) das gepropfte Material anschließend einem Öl einverleibt wird.
2. Verfahren nach Anspruch 1, bei dem das Kohlenwasserstoffpolymer ein hydriertes Copolymer aus Styrol und mindestens einem aliphatischen Dien ausgewählt aus der Gruppe bestehend aus Butadien und Isopren ist.
3. Verfahren nach Anspruch 1, bei dem das Kohlenwasserstoffpolymer ein Copolymer aus Ethylen und einem C_3 - C_{28} - α -Olefin ist.
4. Verfahren nach Anspruch 3, bei dem das Kohlenwasserstoffpolymer im wesentlichen aus Ethylen und Propylen besteht.
5. Verfahren nach Anspruch 4, bei dem das Copolymer im wesentlichen aus 30 bis 80 Gew.-% Ethylen und 20 bis 70 Gew.-% Propylen besteht und ein durchschnittliches zahlenmäßiges Molekulargewicht im Bereich von 10 000 bis 200 000 aufweist.
6. Verfahren nach Anspruch 3, bei dem das Ethylencopolymer ein Terpolymer aus Ethylen, Propylen und einem ungesättigten Dien ist.
7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem eine homogene Mischung des Ethylencopolymers, des ungesättigten Materials, des Initiators und des kettenstoppenden Mittels durch Erhitzen und Mischen bei einer ersten Temperatur unterhalb der Temperatur, bei der der Initiator im wesentlichen freie Radikale erzeugt, gebildet wird und dann bei einer zweiten, höheren Temperatur, bei der der Initiator im wesentlichen freie Radikale erzeugt und ein größerer Teil der Pfropfung stattfindet, erhitzt und gemischt wird.



8. Verfahren nach Anspruch 7, bei dem die erste Temperatur im Bereich von 100 bis 160°C liegt und die zweite Temperatur im Bereich von 170 bis 240°C liegt.
9. Verfahren nach Anspruch 7 oder 8, bei dem das Verfahren in mehreren Stufen ausgeführt wird, wobei die erste Stufe die Bildung der homogenen Mischung bei der ersten Temperatur umfaßt, dann bei der zweiten Temperatur erhitzt und gemischt wird, um Pfropfung zu bewirken, und in mindestens einer zusätzlichen Stufe auf die erste Temperatur gekühlt wird, bei der ersten Temperatur zusätzliches ungesättigtes Material, zusätzlicher Initiator und zusätzliches kettenstoppendes Mittel zugegeben wird und erneut auf die zweite Temperatur erhitzt und gemischt wird, um Pfropfung des zusätzlichen ungesättigten Materials zu bewirken.
10. Verfahren nach Anspruch 3, bei dem das Ethylencopolymer ein bei Raumtemperatur normalerweise fester Kautschuk ist und das Mischen in einem mechanischen Mischer durchgeführt wird, der den Kautschuk, das ungesättigte Material, den Initiator und das kettenstoppende Mittel erhitzt und zu einer homogenen, festen, kautschukartigen Masse knetet, in der die Pfropfung im festen Zustand stattfindet.
11. Verfahren nach einem der Ansprüche 1 bis 10, bei dem das ungesättigte Material Maleinsäureanhydrid ist.
12. Verfahren nach einem der Ansprüche 1 bis 10, bei dem das Stickstoff enthaltende Monomer ausgewählt ist aus der Gruppe bestehend aus Vinylpyridinen, Vinylpyrrolidon, Acrylaten und Methacrylaten.
13. Verfahren nach einem der Ansprüche 1 bis 10, bei dem das ungesättigte Material eine ungesättigte Säure oder ein ungesättigtes Säureanhydrid umfaßt und das resultierende gepfropfte Material weiter mit einem Amin oder Alkohol umgesetzt wird.
14. Verfahren nach einem der Ansprüche 1 bis 11, bei dem das gepfropfte Material in einem Mineral-schmieröl gelöst und mit einem Amin mit 2 bis 60 Kohlenstoffatomen und 1 bis 12 Aminogruppen umgesetzt wird, um ein öllösliches, den Viskositätsindex verbesserndes-Dispergiermittel-Additivkonzentrat zu bilden.
15. Verfahren nach Anspruch 14, bei dem das Amin ein Polyamin mit mindestens einer primären Aminogruppe ist.
16. Verfahren nach einem der Ansprüche 1 bis 15, bei dem die Pfropfreaktion mit zu einer homogenen, festen Masse vermischten Reaktanten durchgeführt wird.
17. Verfahren nach einem der Ansprüche 1 bis 16, bei dem der freiradikalische Initiator ein Peroxid ist.
18. Verfahren nach einem der Ansprüche 1 bis 17, bei dem das kettenstoppende Mittel ein aliphatisches C₄-C₂₄-Mercaptan, Diethylhydroxylamin, Cumol, ein Alkohol oder ein Phenol ist.
19. Verwendung eines gepfropften Materials gemäß einem der Ansprüche 1 bis 18 in einer Schmierölzusammensetzung.
20. Schmierölzusammensetzung gemäß Anspruch 19.

Revendications

1. Procédé de production d'une composition d'huile, qui comprend une huile et un additif dispersant-améliorant l'indice de viscosité, le procédé consistant :
 - (i) à greffer un polymère hydrocarboné d'une oléfine en C₂ à C₂₈, ledit polymère ayant une moyenne numérique du poids moléculaire comprise dans le plage de 5000 à 500 000, avec une matière non saturée choisie dans le groupe comprenant : (A) un acide carboxylique en C₃ à C₁₀ à non-saturation éthylénique portant 1 ou 2 groupes acide carboxylique ou un groupe anhydride, et (B) des monomères à non-saturation éthylénique contenant de l'azote, ayant 6 à 30 atomes de carbone et 1 à 4 atomes d'azote, en présence d'un initiateur de radicaux libres et d'un agent de terminaison



de chaîne, la réaction de greffage étant conduite en atmosphère inerte et principalement en l'absence de solvant chimique, de manière à former une matière greffée utile comme additif dispersant-améliorant l'indice de viscosité,
(ii) à incorporer ensuite la matière greffée à une huile.

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2. Procédé suivant la revendication 1, dans lequel le polymère hydrocarboné est un copolymère hydrogéné de styrène avec au moins un diène aliphatique choisi dans le groupe comprenant le butadiène et l'isoprène.

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3. Procédé suivant la revendication 1, dans lequel le polymère hydrocarboné est un copolymère d'éthylène et d'une alpha-oléfine en C_3 à C_{28} .

4. Procédé suivant la revendication 3, dans lequel le polymère hydrocarboné est essentiellement constitué d'éthylène et de propylène.

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5. Procédé suivant la revendication 4, dans lequel le copolymère est essentiellement constitué de 30 à 80 % en poids d'éthylène et de 20 à 70 % en poids de propylène, et a une moyenne numérique du poids moléculaire comprise dans la plage de 10 000 à 200 000.

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6. Procédé suivant la revendication 3, dans lequel le copolymère d'éthylène est un terpolymère d'éthylène, de propylène et d'un diène non saturé.

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7. Procédé suivant l'une quelconque des revendications 1 à 6, dans lequel un mélange homogène est formé dudit copolymère d'éthylène, d'une matière non saturée, d'un initiateur et d'un agent de terminaison de chaîne par chauffage et agitation à une première température au-dessous de la température à laquelle l'initiateur engendre une quantité importante de radicaux libres, puis chauffage et agitation à une seconde température plus haute à laquelle l'initiateur engendre une quantité notable de radicaux libres, et une proportion dominante dudit greffage a lieu.

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8. Procédé suivant la revendication 7, dans lequel la première température se situe dans la plage de 100 à 160 °C et la seconde température se situe dans la plage de 170 à 240 °C.

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9. Procédé suivant la revendication 7 ou 8, qui est mis en oeuvre par étapes multiples, la première étape consistant à former ledit mélange homogène à la première température, puis à chauffer et à agiter à la seconde température pour effectuer le greffage ; et au moins une étape additionnelle de refroidissement à la première température, d'addition d'un complément de matière non saturée, d'un initiateur et d'un agent de terminaison de chaîne à ladite première température, et d'un nouveau chauffage et d'une agitation à la seconde température pour effectuer le greffage de la matière non saturée additionnelle.

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10. Procédé suivant la revendication 3, dans lequel le copolymère d'éthylène est un caoutchouc normalement solide à la température ambiante et le mélange est effectué dans un mélangeur mécanique qui chauffe et malaxe le caoutchouc, la matière non saturée, l'initiateur et l'agent de terminaison de chaîne en une masse caoutchouteuse solide homogène dans laquelle un greffage a lieu à l'état solide.

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11. Procédé suivant l'une quelconque des revendications 1 à 10, dans lequel la matière non saturée est l'anhydride maléique.

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12. Procédé suivant l'une quelconque des revendications 1 à 10, dans lequel le monomère contenant de l'azote est choisi dans le groupe comprenant des vinylpyridines, des vinylpyrrolidones, des acrylates et des méthacrylates.

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13. Procédé suivant l'une quelconque des revendications 1 à 10, dans lequel la matière non saturée comprend un acide ou anhydride non saturé et la matière greffée résultante est on outre amenée à réagir avec une amine ou un alcool.

14. Procédé suivant l'une quelconque des revendications 1 à 11, dans lequel la matière greffée est dissoute dans une huile lubrifiante minérale et amenée à réagir avec une amine ayant 2 à 60 atomes de carbone et 1 à 12 groupes amino pour former un concentré d'additif dispersant-améliorant l'indice



de viscosité soluble dans l'huile.

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15. Procédé suivant la revendication 14, dans lequel l'amine est une polyamine portant au moins un groupe amino primaire.
16. Procédé suivant l'une quelconque des revendications 1 à 15, dans lequel la réaction de greffage est conduite avec les corps réactionnels malaxés en une masse solide homogène.
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17. Procédé suivant l'une quelconque des revendications 1 à 16, dans lequel l'initiateur de radicaux libres est un peroxyde.
18. Procédé suivant l'une quelconque des revendications 1 à 17, dans lequel l'agent de terminaison de chaîne est un mercaptan aliphatique en C_4 à C_{24} , la diéthylhydroxylamine, le cumène, un alcool ou un phénol.
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19. Utilisation dans une composition d'huile lubrifiante d'une matière greffée suivant l'une quelconque des revendications 1 à 18.
20. Composition d'huile lubrifiante suivant la revendication 19.
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