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# (54) Polymer composition for lubricant additives

(57) A lubricating oil composition containing in combination an acylating agent substituted with a polymer of an alkene with 6 to 40 carbon atoms and an acylating agent substituted with polyisobutylene provides improved viscometric properties for dispersants used in internal combustion engines.

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## Description

### Field of the Invention

**[0001]** The present invention relates to an additive composition comprising in combination an acylating agent substituted with a polymer of an alkene with 6 to 40 carbon atoms; and an acylating agent substituted with polyisobutylene. The invention may be used in lubricating compositions especially for use in internal combustion engines.

### Background of the Invention

**[0002]** It is known to use dispersants in lubricating oils to disperse soot and decrease the accumulation of sludge. Known dispersants include nitrogen containing derivatives of polyisobutylene-substituted succinic acid and derivatives of polydecene. Neither polyisobutylene-substituted succinic acid nor polydecene derivatives exhibit both good low temperature and high temperature viscometrics.

**[0003]** Polyisobutylene-substituted succinic acid based dispersants provide good dispersant properties at high temperature. However, at low temperature, polyisobutylene succinic acid dispersants have poor viscometrics, causing lubricating oils to thicken. To compensate for the poor low temperature viscometrics, viscosity modifiers are added to lubricating oils. The presence of the viscosity modifiers can lead to the potential for soot deposits and the accumulation of sludge.

**[0004]** Polydecene-based dispersants are known for good low temperature viscometric properties, specifically kinematic viscosity and dynamic viscosity. However, at high temperature polydecene-based dispersants are less effective than polyisobutylene-substituted succinic acid based dispersants. Furthermore, polydecene is less attractive as a commercial product due to relatively high costs associated with its production.

**[0005]** GB Patent 1,439,567 discloses liquid organic compositions with detergent properties by reacting a polymer of a straight chain 1-olefin having at least 10 carbons, with maleic anhydride to form the corresponding polyalkenyl succinic anhydride. The polyalkenyl succinic anhydride is then reacted with an alkylene polyamine to form the corresponding polyalkenyl succinimide.

**[0006]** US Patents 4,489,194 and 4,486,573 disclose compositions containing hydrocarbyl substituted carboxylic acylating agents made by reacting, (A) one or more alpha-beta olefinically unsaturated carboxylic acid reagents containing 2 to 20 carbon atoms, exclusive of the carboxyl-based groups with (B) one or more high molecular weight olefin polymers of more than 30 carbon atoms selected from the group consisting of (i) interpolymers of $C_{2-8}$ mono-1-olefins with $C_{12}$-$C_{30}$ mono-olefins, (ii) mixtures of (a) homopolymers and/or interpolymers of $C_{2-8}$ mono-1-olefins with (b) homopolymers and/or interpolymers of $C_{12}$-$C_{30}$ mono-olefins, and (iii) chlorinated or brominated analogs of (i) or (ii). This invention includes the acylated amine and/or alcohol derivatives of these hydrocarbyl-substituted carboxylic acid acylating agents and their use in lubricants and normally liquid fuels.

**[0007]** PCT publication 99/46354 discloses the reaction products of maleic anhydride and oligoalkenes obtained through oligomerisation of linear $C_8$- to $C_{12}$-1-alkenes. The linear $C_8$- to $C_{12}$-1-alkenes contain vinylidene double bond fractions above 30% and have a number average molecular weight from 1000 to 20,000.

**[0008]** It would be desirable to have a composition with dispersancy properties including good high and low temperature viscometrics, capable of improving seal compatability, capable of reducing the amount of volatile oils of lubricating viscosity used and capable of decreasing the accumulation of sludge and/or soot deposits.

### Summary of the Invention

**[0009]** The present invention provides a composition comprising:

(a) an acylating agent containing a substituent of a polymer of an alkene having about 6 to about 40 carbon atoms; and
(b) an acylating agent containing a polyisobutylene substituent;
provided that the weight percent ratio of the alkene polymer substituent to the polyisobutylene substituent in the composition is about 25:75 to about 75:25.

The invention further provides a composition comprising the reaction product of:

(a) an acylating agent containing a substituent of a polymer of an alkene having about 6 to about 40 carbon atoms; and
(b) an acylating agent containing a polyisobutylene substituent; and
at least one compound selected from the group consisting of amines, alcohols, aminoalcohols and mixtures thereof,

provided that the weight percent ratio of the alkene polymer substituent to the polyisobutylene substituent in the composition is about 25:75 to about 75:25.

**[0010]** The invention further provides a composition comprising:

(a) an acylating agent containing a substituent of a polymer of an alkene having 6 to 11 carbons atoms; and
(b) an acylating agent containing a polyisobutylene substituent;
provided that the weight percent ratio of the polyalkene substituent to the polyisobutylene substituent in the composition is about 5:95 to about 95:5.

**[0011]** The invention further provides a method for preparing an acylating agent composition, comprising reacting a carboxylic acid reactant with a mixture of an alkene polymer of 6 to about 40 carbon atoms and a polyisobutylene, wherein the weight ratios of the alkene polymer and the polyisobutylene employed are about 25:75 to about 75:25.

**[0012]** The invention further provides a method for preparing an acylating agent composition, comprising reacting a carboxylic acid reactant with an alkene polymer of 6 to about 40 carbon atoms, and separately reacting a carboxylic acid reactant with a polyisobutylene, and subsequently combining the reaction products; wherein the weight ratios of the alkene polymer and the polyisobutylene employed are about 25:75 to about 75:25.

**[0013]** The invention further provides a method for preparing a dispersant composition, comprising mixing together:

the reaction product of an acylating agent containing a substituent of a polymer of an alkene having about 6 to about 40 carbon atoms with an amine, alcohol, aminoalcohol, or mixtures thereof; and
the reaction product of an acylating agent containing a polyisobutylene substituent with an amine, alcohol, aminoalcohol, or mixtures thereof;
provided that the weight percent ratio of the alkene polymer substituent to the polyisobutylene substituent in the composition is about 25:75 to about 75:25.

**[0014]** The invention further provides a method for lubricating an internal combustion engine, comprising supplying thereto a lubricant comprising the composition as described herein.

**[0015]** The present invention further provides a composition capable of providing good high temperature and low temperature viscometrics. It can further lead to a decrease in sludge accumulation and soot deposits. It further provides compositions capable of decreasing the amount of viscosity modifier in lubricating oils. It further provides compositions capable of reducing the amount of volatile oils of lubricating viscosity used and capable of imparting improved seal compatability.

## Detailed Description of the Invention

**[0016]** In one aspect, the composition of the present invention comprises:

(a) an acylating agent containing a substituent of a polymer of an alkene having about 6 to about 40 carbon atoms; and
(b) an acylating agent containing a polyisobutylene substituent;
provided that the weight percent ratio of the alkene polymer substituent to the polyisobutylene substituent in the composition is about 25:75 to about 75:25.

**[0017]** Preferably the weight percent ratio of alkene polymer to polyisobutylene ratio is 30:70 to 70:30, more preferably 35:65 to 65:35, more preferably 40:60 to 60:40 and most preferably 45:55 to 55:45.

**[0018]** The alkene comprises carbon atoms ranging from a lower value of carbon atoms of 6, 7, 8, 9 or 10; and an upper value of 40, 30, 20, 18, 16, 14 or 11 carbon atoms, or any combinations of lower and higher values, e.g., 6-40, 6-20, 6-11, 8-40, 8-20, or 8-11.

**[0019]** In an alternative embodiment, the composition comprises:

an acylating agent substituted with a polymer of an alkene having 6 to 11 carbons atoms; and
an acylating agent substituted with a polyisobutylene; provided that the weight percent ratio of the alkene polymer to the polyisobutylene in the composition is 5:95 to 95:5.

**[0020]** Preferably the alkene polymer with 6 to 11 carbons atoms and the polyisobutylene are present in a weight ratio of 10:90 to 90:10, more preferably, 20:80 to 80:20, more preferably 25:75 to 75 to 25, even more preferably 30:70 to 70:30, even more preferably 35:65 to 65:35, even more preferably 40:60 to 60:40 and most preferably 45:55 to

55:45.

**[0021]** The polyalkene preferably contains a vinylidene double bond. Preferably the fraction of polyalkene molecules containing the vinylidene double bond is at least 25%, more preferably at least 30%, even more preferably at least 45%, even more preferably at least 55% and most preferably at least 70%.

**[0022]** Examples of suitable alkenes include monomers selected from the group consisting of 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-henicosene, 1-docosene, 1-tetracosene, 1-pentacosene, 1-hexacosene, 1-octacosene, 1-nonacosene and mixtures thereof. A preferred alkene is 1-decene.

**[0023]** Polyisobutylene is derived from isobutylene. It preferably contains a vinylidene double bond. Preferably the fraction of polyisobutylene molecules containing a vinylidene double bond is at least 25%, more preferably at least 30%, even more preferably at least 45%, even more preferably at least 55% and most preferably at least 70%.

**[0024]** The number average molecular weight of the substituents (a) and (b) of the invention can be controlled using a variety of techniques such as reaction temperature, initiators, monomer concentration and type of chain transfer agent. The number average molecular weight of the substituents of each (a) and (b) is preferably 350 to 25,000, more preferably 500 to 15,000, and most preferably 1,000 to 5,000.

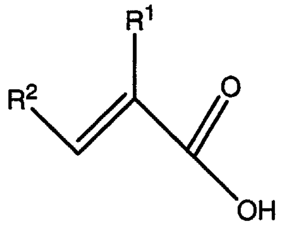
**[0025]** As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);
(2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);
(3) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulphur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

Acylating Agents

**[0026]** The acylating agents (which are substituted by the above-described polymers) include monobasic or polybasic carboxylic acids or reactive equivalents thereof. Reactive equivalents of carboxylic acids include anhydrides, esters, acylated nitrogen, acyl halide, nitriles, metal salts or mixtures thereof. Among these, anhydrides, particularly of diacids, are preferred.

Monobasic carboxylic acids include those represented by the formula:



(I)

wherein $R^1$ is hydrogen or hydrocarbyl containing 1 to 20, preferably 1 to 10, more preferably 1 to 5 and most preferably 1 to 2 carbon atoms; and $R^2$ is hydrogen or alkyl with 1 to 6, preferably 1 to 4 and most preferably 1 to 2 carbon atoms.

**[0027]** Monobasic carboxylic acids and derivatives thereof include (meth)acrylic acid, cinnamic acid, crotonic acid, 3-phenylpropenoic acid, α,β-decenoic acid, glyoxylic acid and mixtures thereof. (The expression "(meth)acrylic" is intended to encompass both acrylic and methacrylic.)

**[0028]** Dibasic carboxylic acids and derivatives thereof include fumaric acid, maleic acid, mesaconic acid, itaconic acid, and citraconic acid. In one embodiment the derivative of a dibasic carboxylic acid is maleic anhydride.

**[0029]** In one embodiment the carboxylic acid includes glyoxylic acid or an ester thereof, or the hemiacetals of any of them. A preferred class of glyoxylic acid derivatives are glyoxylic acid esters. Examples of suitable glyoxylic acid esters include methyl glyoxylate, ethyl glyoxylate, n-propyl glyoxylate, isopropyl glyoxylate, n-butyl glyoxylate, isobutyl glyoxylate, pentyl glyoxylate, hexyl glyoxylate, heptyl glyoxylate, octyl glyoxylate, nonyl glyoxylate, decyl glyoxylate, undecyl glyoxylate, dodecyl glyoxylate, tridecyl glyoxylate, tetradecyl glyoxylate, pentadecyl glyoxylate, hexadecyl glyoxylate, heptadecyl glyoxylate, octadecyl glyoxylate, nonadecyl glyoxylate, icosyl glyoxylate, stearyl glyoxylate, palmityl glyoxylate, hemiacetal glyoxylate esters such as glyoxylic methanol ester hemiacetals and mixtures thereof.

**[0030]** Preferred acylating agents are selected from the group consisting of maleic acid, maleic anhydride, (meth) acrylic acid, itaconic acid, fumaric acid, glyoxylic acid and mixtures thereof.

**[0031]** In one aspect of the present invention the composition comprises the reaction product of:

(a) an acylating agent containing a substituent of a polymer of an alkene having about 6 to about 40 carbon atoms; and
(b) an acylating agent containing a polyisobutylene substituent; and
(c) at least one compound selected from the group consisting of amines, alcohols, aminoalcohols and mixtures thereof,

provided that the weight percent ratio of the alkene polymer substituent to the polyisobutylene substituent in the composition is about 25:75 to about 75:25

Process

**[0032]** The compositions of the invention can be prepared using the following methods:

(I) For preparing an acylating agent composition, reacting a carboxylic acid reactant with a mixture of an alkene polymer of 6 to about 40 carbon atoms and a polyisobutylene, wherein the weight ratios of the alkene polymer and the polyisobutylene employed are about 25:75 to about 75:25.

(II) For preparing an acylating agent composition, reacting a carboxylic acid reactant with an alkene polymer of 6 to about 40 carbon atoms, and separately reacting a carboxylic acid reactant with a polyisobutylene, and subsequently combining the reaction products; wherein the weight ratios of the alkene polymer and the polyisobutylene employed are about 25:75 to about 75:25

(III) For preparing a dispersant composition, mixing together:

the reaction product of an acylating agent containing a substituent of a polymer of an alkene having about 6 to about 40 carbon atoms with an amine, alcohol, aminoalcohol, or mixtures thereof; and

the reaction product of an acylating agent containing a polyisobutylene substituent with an amine, alcohol, aminoalcohol, or mixtures thereof;

provided that the weight percent ratio of the alkene polymer substituent to the polyisobutylene substituent in the composition is about 25:75 to about 75:25.

The methods (I), (II) and (III) are typically conducted in the temperature range of 100°C to 300°C, preferably 130°C to 270°C and more preferably 150°C to 250°C.

In one embodiment, the methods (I) and (II) may contain a halogen selected from the group consisting of chlorine, bromine, iodine and mixtures thereof. The reactions carried out in the presence of halogen can take place in the temperature range of 100°C to 300°C, preferably 110°C to 250°C and more preferably 120°C to 220°C.

(IV) The invention further includes a method for reacting (I) or (II) with compounds selected from the group consisting of amines, alcohols, aminoalcohols and mixtures thereof. The resulting product has dispersant properties.

Reaction Products with Amines, Alcohols and Aminoalcohols

**[0033]** Amines suitable for reacting with the mixture (a) and (b) include monoamines and polyamines, preferably polyamines. The polyamines may be linear or branched and are selected from the group consisting of alkylenepolyamine, cycloaliphatic polyamine, heterocyclic polyamines and mixtures thereof.

**[0034]** In one embodiment the alkylenepolyamines are selected from the group consisting of ethylenepolyamines, propylenepolyamines, butylenepolyamines and mixtures thereof. Examples of propylenepolyamines include propylenediamine, dipropylenetriamine or mixtures thereof. Ethylenepolyamines are preferred and specific compounds include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyamine still bottoms and so-called "heavy amines" such as HPA-X™ from Union Carbide and E-100™ from Dow, and mixtures thereof.

**[0035]** In one embodiment the polyamines are α,β-diaminoalkanes. Suitable α,β-diaminoalkanes include diaminopropanes, diaminobutanes or mixtures thereof. Specific diaminoalkanes are selected from the group consisting of N-(2-aminoethyl)-1,3-propane diamine, 3,3'-diamine-N-methyldipropylamine, tris(2-amino-ethyl)amine, N,N-bis (3-aminopropyl)-1,3-propane diamine, N,N'-1,2-ethanediylbis-(1,3-propane diamine) and mixtures thereof.

**[0036]** Other suitable polyamines include di-(trimethylene)triamine, piperazine, diaminocyclohexanes and mixtures thereof.

**[0037]** Alcohols suitable for reacting with the mixture (a) and (b) include monohydric and polyhydric alcohols. Polyhydric alcohols are preferred with 2 to 10, preferably 2 to 6 hydroxy groups. The alcohols can be aliphatic, cycloaliphatic, aromatic, or heterocyclic.

**[0038]** Suitable alcohols include dihydroxypropanes, dihydroxybutanes, dihydroxy-pentanes, glycerine, trihydroxypropanes, trihydroxybutanes, trihydroxypentanes and mixtures thereof.

**[0039]** In one embodiment the preferred alcohol is a polyol. Suitable polyols include ethylene glycol, propylene glycol, butylene glycol, pentaerthyritol, mannitol, sorbitol, glycerol, erythritol, 2-hydroxymethyl-2-methyl-1,3-propanediol (trimethylolethane), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (trimethylolpropane), 1,2,4-hexanetriol and mixtures thereof.

**[0040]** Aminoalcohols suitable for the invention contain 1 to 6 and preferably 1 to 3 hydroxy groups; and 1 to 8 and preferably 1 to 2 amine groups.

**[0041]** The aminoalcohols of the invention can be selected from the group consisting of ethanolamine, isopropanolamine, diethanolamine, triethanolamine, diethylethanolamine, dimethylethanolamine, dibutylethanolamine, 3-amino-1,2-propanediol; serinol; 2-amino-2-methyl-1,3-propanediol; tris(hydroxymethyl)-aminomethane; 1-amino-1-deoxy-D-sorbitol; diethanol amine; diisopropanolamine; N-methyl-N,N-diethanol amine; triethanolamine; N,N,N',N'-tetrakis(2-hydroxypropyl)ethylene-diamine, 2-amino-2-methyl-1-propanol, 2-dimethylamino-methyl-1-propanediol, 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methyl-1,3-propanediol, 2-amino-1-butanol and mixtures thereof. Preferably the aminoalcohol is ethanolamine.

## Oil of Lubricating Viscosity

**[0042]** The composition of the present invention can be added to an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, hydrofinishing, unrefined, refined and re-refined oils, and mixtures thereof.

**[0043]** Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

**[0044]** Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

**[0045]** Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

**[0046]** Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g., castor oil, lard oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types and oils derived from coal or shale or mixtures thereof.

**[0047]** Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerised and interpolymerised olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulphides and the derivatives, analogs and homologs thereof and mixtures thereof. Polyalphaolefins are typically hydrogenated when used as lubricating oils.

**[0048]** Other synthetic lubricating oils include but are not limited to liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), and polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes.

**[0049]** Oils of lubricating viscosity can also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulphur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80-120); Group II (sulphur content ≤0.03 wt %, and ≥90 wt % saturates, viscosity index 80-120); Group III (sulphur content ≤0.03 wt %, and ≥90 wt % saturates, viscosity index ≥120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). Preferably the oil of lubricating viscosity is selected from an API Group II, Group III, Group IV, Group V oil and mixtures thereof.

**[0050]** The oil of lubricating viscosity is typically present at 30 to 99.9, preferably 55 to 99, and more preferably 65 to 96 and most preferably 73 to 95 weight percent of the lubricating oil composition.

**[0051]** In a typical lubricating composition comprising, the compositions of the invention can be present in an oil of lubricating viscosity in amounts of 0.1 to 30, preferably 0.5 to 20, more preferably 1 to 15, and most preferably 5 to 12 weight percent of the lubricating oil composition.

**[0052]** If the present invention is in the form of a concentrate (which can be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of each of the above-mentioned dispersant, as well as other components, to diluent oil is typically in the range of 99:1 to 10:90 by weight.

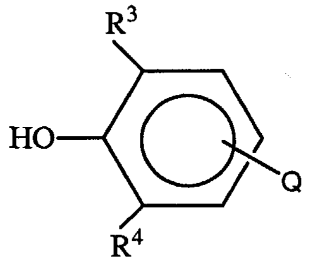
## Optional Additives

**[0053]** Optionally the lubricating composition can include additives selected from the group consisting of antioxidants, metal deactivators, detergents, antiwear agents, dispersants, antiscuffing agents, extreme pressure agents, foam inhibitors, demulsifiers, viscosity modifiers, pour point depressants and mixtures thereof.

**[0054]** The total combined amount of the optional additives present can be 0 to 40, preferably 0.5 to 25, more preferably 3 to 20 and most preferably 5 to 15 weight percent of the lubricating oil composition.

## Antioxidants

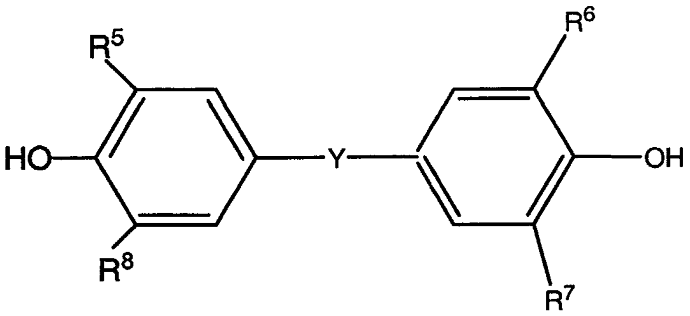
**[0055]** Antioxidants include hindered phenols represented by the formula:



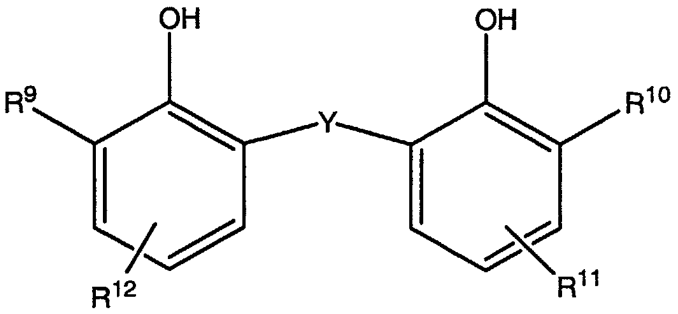
(II)

wherein $R^3$ and $R^4$ are independently branched or linear alkyl groups containing about 1 to 24, preferably 4 to 18, and most preferably 4 to 12 carbon atoms. $R^3$ and $R^4$ can be either straight or branched chain; branched is preferred. Preferably the phenol is butyl substituted containing two t-butyl groups. When the t-butyl groups occupy the 2,6-positions, the phenol is sterically hindered. Q is hydrogen or hydrocarbyl. Examples of suitable hydrocarbyl groups include 2-ethylhexyl, n-butyl, dodecyl or mixtures thereof.

**[0056]** Other optional sterically hindered phenols suitable for the invention include those represented by the formulae:



(III)

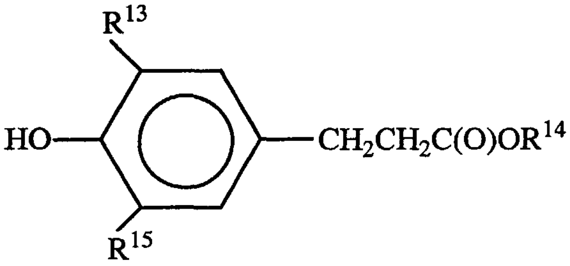


(IV)

wherein $R^5$, $R^6$, $R^7$, $R^8$, $R^9$, $R^{10}$ are either straight or branched chain and contain 4 to 18, preferably 4 to 12 carbon atoms. Preferably the phenol is butyl substituted. $R^{11}$ and $R^{12}$ are independently hydrogen or hydrocarbyl; preferably $R^{11}$ and $R^{12}$ are arylalkyl or alkyl groups. The alkyl groups can be linear or branched, linear being preferred. $R^{11}$ and $R^{12}$ are preferably in the para position. The arylalkyl or alkyl groups typically contain 1 to 15, preferably 1 to 10, and more preferably 1 to 5 carbon atoms. The bridging group Y includes $-CH_2-$ (methylene bridge) or $-CH_2OCH_2-$ (ether bridge).

**[0057]** Examples of methylene-bridged sterically hindered phenols include 4,4'-methylene-bis-(6-tert-butyl o-cresol), 4,4 -methylene-bis-(2-tert-amyl-o-cresol), 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol), 4,4-methylene-bis-(2,6-di-tertbutyl-phenol) and mixtures thereof.

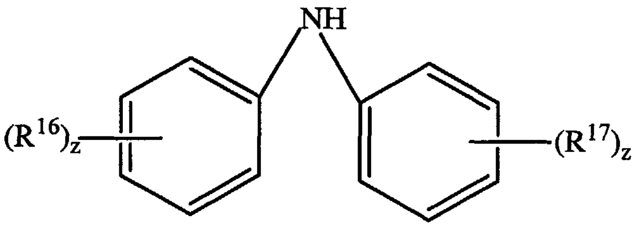
**[0058]** In one embodiment the antioxidant is a hindered ester-substituted phenol represented by the formula:



(V)

wherein $R^{13}$, $R^{14}$ and $R^{15}$ are straight or branched alkyl group containing 2 to 22, preferably 2 to 18, more preferably 4 to 8 carbon atoms. Specific examples include of alkyl groups include 2-ethylhexyl or n-butyl ester, dodecyl and mixtures thereof.

**[0059]** Another class of antioxidant is alkylated diphenylamines that can be represented by the following formula:



(VI)

wherein $R^{16}$ and $R^{17}$ are independently hydrogen or hydrocarbyl, preferably arylalkyl or alkyl groups. The arylalkyl groups contain 5 to 20, preferably 6 to 10 carbons atoms. The alkyl groups can be linear or branched, preferably linear; the alkyl group contains 1 to 24, preferably 2 to 18 and most preferably 4 to 12 carbon atoms; and z is independently 0, 1, 2, or 3, provided that at least one aromatic ring contains a hydrocarbyl group. Preferred alkylated diphenylamines include bis-nonylated diphenylamine and bis-octylated diphenylamine and mixtures thereof.

## Metal Deactivators

**[0060]** Metal deactivators can be used to neutralise the catalytic effect of metal for promoting oxidation in lubricating oil. Examples of metal deactivators include derivatives of benzotriazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, 2-alkyl-dithiobenzothiazoles, 2-(N,N-dialkyldithiocarbamoyl)benzothiazoles, 2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles, 2,5-bis(N,N-dialkyldithiocarbamoyl)-1,3,4-thiadiazoles, 2-alkyldithio-5-mercapto thiadiazoles and mixtures thereof.

**[0061]** Preferably the metal deactivator is a hydrocarbyl substituted benzotriazole compound. The benzotriazole compounds can include hydrocarbyl substitutions in at least one of the following ring positions 1- or 2- or 4- or 5- or 6- or 7-. The hydrocarbyl groups contain about 1 to about 30, preferably about 1 to about 15, more preferably about 1 to about 7 carbon atoms, most preferably the metal deactivator is 5-methylbenzotriazole, which may be used alone or in combination.

## Detergents

**[0062]** Detergents are well-known and include neutral or overbased, carbonated or non-carbonated Newtonian or non-Newtonian, basic salts of alkali, alkaline earth and transition metals with one or more hydrocarbyl sulphonic acid, carboxylic acid, phosphorus acid, mono- and/or di- thiophosphorus acid, alkyl phenol, sulphur coupled alkyl phenol compounds, salixarates, saligenins or mixtures thereof. Commonly used metals are sodium, potassium, calcium, magnesium, lithium or mixtures thereof. Most commonly used metals include sodium, magnesium, calcium and mixtures thereof. Overbased detergents are disclosed for instance in US Patent 3,629,109.

## Dispersants

**[0063]** Dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition, they do not contain ash-forming metals; and they do not normally contribute any ash forming metals when added to a lubricant. Ashless type dispersants are characterised by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. Examples of N-substituted long chain alkenyl succinimides include polyisobutylene succinimide with number average molecular weight in the range 350 to 5000, preferably 500 to 3000. Succinimide dispersants and their preparation are disclosed, for instance, in US Patent 4,234,435.

## Antiwear Agents

**[0064]** The lubricant may additionally contain an antiwear agent. Useful antiwear agents include metal thiophosphates, especially zinc dialkyldithiophosphates; phosphoric acid esters or salt thereof; phosphites; and phosphorus-containing carboxylic esters, ethers, and amides.

## Antiscuffing Agents

**[0065]** The lubricant may also contain an antiscuffing agent. Antiscuffing agents that decrease adhesive wear are often sulphur containing compounds. Typically the sulphur containing compounds include organic sulphides and polysulphides, such as benzyldisulphide, bis-(chlorobenzyl) disulphide, dibutyl tetrasulphide, di-tertiary butyl polysulphide, sulphurised sperm oil, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, sulphurised Diels-Alder adducts, alkyl sulphenyl N'N-dialkyl dithiocarbamates, the reaction product of polyamines with polybasic acid esters, chlorobutyl esters of 2,3-dibromo-propoxyisobutyric acid, acetoxymethyl esters of dialkyl dithiocarbamic acid and acyloxyalkyl ethers of xanthogenic acids or mixtures thereof.

## Extreme Pressure Agents

**[0066]** Extreme Pressure (EP) agents that are soluble in the oil include sulphur and chlorosulphur-containing EP agents, chlorinated hydrocarbon EP agents, phosphorus EP agents, and mixtures thereof. Examples of such EP agents include compounds selected from the group consisting of chlorinated wax, organic sulphides and polysulphides, such as benzyldisulphide, bis-(chlorobenzyl) disulphide, dibutyl tetrasulphide, sulphurised sperm oil, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, and sulphurised Diels-Alder adducts; phosphosulphurised hydrocarbons, such as the reaction product of phosphorus sulphide with turpentine or methyl oleate, phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, *e.g.*, dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite, metal thiocarbamates, such as zinc dioctyldithiocarbamate and barium heptylphenol diacid, such as zinc dicyclohexyl phosphorodithioate and the zinc salts of a phosphorodithioic acid; amine salts of alkyl and dialkylphosphoric acids, including, for example, the amine salt of the reaction product of a dialkyldithiophosphoric acid with propylene oxide; and mixtures thereof.

## Foam Inhibitors

**[0067]** Foam inhibitors are known and include organic silicones such as polyacetates, dimethyl silicone, polysiloxanes, polyacrylates or mixtures thereof. Examples of foam inhibitors include polyethylacrylate, poly-2-ethylhexylacrylate, polyvinylacetate and mixtures thereof.

## Demulsifiers

**[0068]** Demulsifiers are known and include derivatives of propylene oxide, ethylene oxide, polyoxyalkylene alcohols, alkyl amines, amino alcohols, diamines or polyamines reacted sequentially with ethylene oxide or substituted ethylene oxides or mixtures thereof. Examples of demulsifiers include polyethylene glycols, poly(ethyleneoxides), poly(propylene oxides), (ethylene oxide-propylene oxide) polymers and mixtures thereof.

## Pour Point Depressants

**[0069]** Pour point depressants are known and include esters of maleic anhydride-styrene copolymers, polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkylfumarates, vinyl esters of fatty acids, ethylene-vinyl acetate copolymers, alkyl phenol formaldehyde condensation resins, alkyl vinyl ethers and mixtures thereof.

## Viscosity Modifiers

**[0070]** Viscosity modifiers are known and include copolymers of styrene-butadiene rubbers, ethylene-propylene polymers, polyisobutenes, hydrogenated styreneisoprene polymers, hydrogenated radical isoprene polymers, polymethacrylate acid esters, polyacrylate acid esters, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins, polyalkylmethacrylates, esters of maleic anhydride-styrene copolymers or mixtures thereof.

## Industrial Application

**[0071]** The compositions of the present invention are useful as additives in greases, gear oils, industrial fluids, hydraulic fluids, transmission fluids, turbine oils, circulating oils, and engine oils. They are particularly useful in lubricants for internal combustion engines, such as diesel fuelled engines or gasoline fuelled engines. Such engines can be lubricated by supplying thereto a lubricating oil composition comprising the components as described above.

**[0072]** The use of the lubricating oil compositions of the invention in internal combustion engines will typically exhibit at least one improved property selected from the group consisting of good high temperature viscometrics, low temperature viscometrics, decrease in sludge accumulation, decrease in soot deposits, improved seal compatability, reduced amount of volatile oils of lubricating viscosity and a decrease in amount of viscosity modifier required, and improved seal compatability. Improved seal compatibility can be revealed by improved tensile strength, improved elongation strength and decreased hardness.

**[0073]** The following examples provide an illustration of the invention. These examples are non exhaustive and are not intended to limit the scope of the invention.

## Examples

### Examples 1 to 3 and Reference Examples R1 and R2

**[0074]** Mixtures of polydecene (obtained from BP Amoco) with number average molecular weight of 1656 and high vinylidene polyisobutylene with number average molecular weight of 1510 are reacted with maleic anhydride. The mixtures of high vinylidene polydecene and high vinylidene polyisobutylene contain approximately 1600g of sample with weight ratios of polydecene: polyisobutylene of 1600:0, 1200:400, 800:800, 400:1200 and 0:1600 and are reacted with approximately 213.9g of maleic anhydride. The reactants are heated to 203°C over 3 1/2 hours and held at this temperature for twenty-four hours. The product of the reaction is then heated to 210°C for one hour under vacuum at 0.67 kPa (5mm Hg) to remove volatiles.

**[0075]** Approximately 600g of the above reaction product is dissolved in diluent oil and heated to 110°C under nitrogen. Approximately 34g of HPAX™(polyamine still bottoms) is added over 30 minutes and the reaction mixture is held at 110°C for a further 30 minutes. The reaction is heated to 155°C and held for 5 hours. The resulting product is cooled and filtered to produce a dispersant.

**[0076]** The dispersant is dissolved in a 5W-30 lubricating oil prepared containing 68.9 weight percent of Yubase™ 3050 API Group 3 base oil, 5 $mm^2s^{-1}$ (cSt) at 100°C and 31.1 weight percent of PAO-6 Group 4 base oil, 6 $mm^2s^{-1}$ (cSt) at 100°C. Reference examples 1 and 2 contain 100wt % of polyisobutylene succinimide and 100wt % of polydecene succinimide respectively. Examples 1 to 3 contain polyisobutylene succinimide: polydecene succinimide weight percent ratios of 25:75, 50:50 and 75:25 respectively.

### Examples 4 to 6 and Reference Examples R3 and R4

**[0077]** These samples are prepared in a similar process to examples 1 to 3 and reference examples R1 to R2 except they are dissolved in Exxon 100N base oil at 0.5 wt%.

### Examples 7 to 10 and Reference Examples R5 to R8

**[0078]** These samples are prepared in a similar process to example 5 except, 7 to 10 wt% of lubricating oil composition contains a 50:50 mixture of the polyisobutylene: polydecene dispersant. Reference examples R5 to R8 contain 7 to 10 wt% of a polyisobutylene dispersant in 5W-30 grade lubricating oil compositions containing 56 weight percent of API Group 4, PAO-4 base oil, 4 $mm^2s^{-1}$ (cSt) at 100°C, 30 weight percent of API Group 4, PAO-6 base oil, 6 $mm^2s^{-1}$ (cSt) at 100°C and 13.6 weight percent of PL 3970 API Group 5 base oil, 4.5 $mm^2s^{-1}$ (cSt) at 100°C.

Test **1**: Seal Performance

**[0079]** Seal compatibility tests are designed to evaluate the effect of motor oils on Parker-Pradifa™ FKM E-281 seal elastomers (fluoroelastomer). Six dumbbells of elastomer are suspended using a micro wire and glass separators are covered by at least 10 ml of oil. The test vessel is covered with aluminium foil and stored at 150°C for 96 hours. The elastomer is removed from the oil and tested for percentage change in tensile strength, elongation at break, cracking (by bending) and hardness. The results obtained for examples 1 to 3 and comparative examples 1 and 2 are:

| Ex. | Mixture | | Final Seal Test Values | | | |
|---|---|---|---|---|---|---|
| | Wt % Polydecene | Wt% Polyisobutylene | Cracking | Tensile | Elongation (%) | Hardness (%) |
| R1 | 0 | 100 | Mild | 8.1 | 170.0 | 71.0 |
| 1 | 25 | 75 | None | 8.5 | 172.2 | 71.0 |
| 2 | 50 | 50 | Barely | 10.0 | 206.6 | 70.5 |
| 3 | 75 | 25 | Barely | 8.2 | 175.6 | 71.0 |
| R2 | 100 | 0 | Moderate | 7.8 | 168.8 | 72.2 |

The analysis indicates seals treated with compositions containing a weight percent ratio of polydecene to polyisobutylene 25:75 to 75:25 have decreased amounts of cracking compared with comparative examples 1 and 2. Furthermore, other seal properties such as tensile strength, elongation and hardness are improved when compositions containing a weight percent ratio of polydecene to polyisobutylene 25:75 to 75:25 are used. Overall the analysis indicates dispersants of the invention provide improved seal properties compared with conventional dispersants.

Test 2: Sludge Performance

**[0080]** A dispersant sample is dissolved in Exxon 100N diluent oil at six concentrations between 0.125 wt% and 0.004 wt% and mixed with a sludge sample. The resulting mixture is allowed to stand for 24 hours. The amount of sludge remaining in solution at the lowest concentration of dispersant is measured.

**[0081]** The sludge ratio is calculated by dividing the amount of sludge by the weight percent of the dispersant used. The higher the sludge ratio indicates a lower concentration of dispersant is better able to keep the sludge in solution. The results obtained for examples 1 to 3 and comparative examples 1 and 2 are:

| Example | Mixture | | Sludge Ratio |
|---|---|---|---|
| | Wt % Polydecene | Wt % Polyisobutylene | |
| R3 | 0 | 100 | 225 |
| 4 | 25 | 75 | 225 |
| 5 | 50 | 50 | 175 |
| 6 | 75 | 25 | 125 |
| R4 | 100 | 0 | 63 |

**[0082]** The analysis indicates compositions with weight percent ratios of polydecene to polyisobutylene between 25:75 and 75:25 have good dispersancy properties. Furthermore, better results are obtained when the polydecene to polyisobutylene is between 25:75 and 50:50.

Test 3: High Temperature Viscometrics at Constant Treat Rates

**[0083]** The KV100 (kinematic viscosity) value is determined by measuring the time for 40g of oil to flow under gravity through a calibrated glass capillary viscometer.

**[0084]** Examples 4-6 and comparative examples R3-R4 demonstrate the high temperature viscometrics for compositions of the invention with a dispersant treat rate held at 9wt %. The results obtained are:

| Example | Mixture | | |
|---|---|---|---|
| | Wt % Polydecene | Wt% Polyisobutylene | KV100°C |
| R3 | 0 | 100 | 13.10 |
| 4 | 25 | 75 | 12.73 |
| 5 | 50 | 50 | 12.01 |
| 6 | 75 | 25 | 11.69 |
| R4 | 100 | 0 | 11.01 |

**[0085]** The analysis indicates only examples with polydecene substituent in the dispersant composition maintain KV100°C at 12.5 $mm^2s^{-1}$ (cSt) or less. By interpolating the KV100°C data, approximately 31wt % of polydecene substituent is required in dispersant compositions with a 9 wt% treat rate to maintain KV100°C at 12.5 $mm^2s^{-1}$ (cSt) or less.

Test 4: High Temperature Viscometrics at Varied Treat Rates

**[0086]** Experimental procedure is as is described in Test 3. The results obtained for examples 7 to 10 and reference examples R5-R8 are:

| Example | Wt % Dispersant | KV100°C |
|---|---|---|
| R5 | 7 | 12.03 |
| R6 | 8 | 12.63 |
| R7 | 9 | 13.1 |
| R8 | 10 | 13.68 |
| 7 | 7 | 11.13 |
| 8 | 8 | 11.69 |
| 9 | 9 | 12.01 |
| 10 | 10 | 12.44 |

**[0087]** The analysis indicates to keep the oil at a viscosity of 12.5 $mm^2s^{-1}$ (cSt) or less, the maximum amount of polyisobutylene-only type dispersants (reference examples R5-R8) that can be used is 7wt % (example R5). However, using dispersant compositions of the invention with a wt % ratio of polyisobutylene: polydecene of 50:50 allows the amount of dispersant to be increased to 10wt% (example 9).

**[0088]** Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

**[0089]** While the invention has been explained, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

## Claims

**1.** A composition comprising:

(a) an acylating agent containing a substituent of a polymer of an alkene having 6 to 40 carbon atoms; and
(b) an acylating agent containing a polyisobutylene substituent;
provided that the weight percent ratio of the alkene polymer substituent to the polyisobutylene substituent in the composition is 25:75 to 75:25.

**2.** The composition of claim 1 wherein the alkene comprises a mixtures of alpha-olefins.

**3.** The composition of claim 1 or claim 2 wherein the alkene contains 6 to 11 carbon atoms.

**4.** A composition comprising:

(a) an acylating agent containing a substituent of a polymer of an alkene having 6 to 11 carbons atoms; and
(b) an acylating agent containing a polyisobutylene substituent;
provided that the weight percent ratio of the alkene polymer substituent to the polyisobutylene substituent in the composition is 5:95 to 95:5.

**5.** The composition of either of claims 3 and 4 wherein the alkene polymer with 6 to 11 carbons atoms comprises polydecene.

**6.** A composition comprising the reaction product of the composition of any one of the preceding claims with an amine, an alcohol, an aminoalcohol, or mixtures thereof.

**7.** The composition of any one of the preceding claims further comprising at least one additive selected from the group consisting of antioxidants, metal deactivators, detergents, dispersants, antiwear agents, antiscuffing agents, extreme pressure agents, foam inhibitors, demulsifiers, viscosity modifiers, pour point depressants and mixtures thereof.

**8.** The composition of any one of the preceding claims further comprising an oil of lubricating viscosity.

**9.** A method for lubricating an internal combustion engine, comprising supplying thereto the composition of claim 8.

**10.** A method for preparing an acylating agent composition, comprising reacting
a carboxylic acid reactant with
an polymer of an alkene of 6 to 40 carbon atoms and a polyisobutylene, wherein the weight ratios of the

alkene polymer and the polyisobutylene employed are 25:75 to 75:25.

**11.** The method of claim 10 wherein a fraction of the alkene polymer molecules and of the polyisobutylene molecules contain a vinylidene double bond.

**12.** The method of either of claims 10 and 11, wherein a carboxylic acid reactant is reacted with an alkene polymer of 6 to 40 carbon atoms,
separately a carboxylic acid reactant is reacted with a polyisobutylene,
and the products of each reaction are subsequently combined.

**13.** The method of either of claims 10 and 11, wherein the carboxylic acid reactant is reacted with a mixture of an alkene of 6 to 40 carbon atoms and a polyisobutylene.

**14.** The method of any one of claims 10 - 13, wherein the acylating agent composition is further reacted with an amine, an alcohol, an aminoalcohol, or mixtures thereof.

**15.** The method of claim 14 wherein the carboxylic acid and the alkene polymer of 6 to 40 carbon atoms and the reaction products of the carboxylic acid and the polyisobutylene are further reacted with an amine, an alcohol, an aminoalcohol, or mixtures thereof, and the reaction products thereof are mixed together.

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## EUROPEAN SEARCH REPORT

Application Number
EP 04 25 1893

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| Place of search | Date of completion of the search | Examiner |
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CATEGORY OF CITED DOCUMENTS

X : *particularly relevant if taken alone*
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L : document cited for other reasons
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