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(74) Agent: BORDEN LADNER GERVAIS LLP

(71) Demandeur/Applicant:
SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V., NL

(72) Inventeurs/Inventors:
CRANE, ANTHONY E., GB;
SHAW, ROBERT WILLIAM, GB;
SCOTT, RICHARD MARK, GB

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(71) Applicant: SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; carel Van Bylandtlaan 30, NL-2596 HR The Hague (NL).
(72) Inventors: SCOTT, Richard, Mark; Hamlet Court, Heart's Delight, Borden, Sittingbourne, Kent ME9 8HX (GB). SHAW, Robert, William; 89 Gadby Road, Sittingbourne, Kent ME10 1PY (GB). CRANE, Anthony, E; l Gorse Field, Tattenhall, Cheshire CH3 9HB (GB).
(74) Agent: MANSELL, Keith, Rodney; PO Box 1, Milton Hill, Abingdon, Oxfordshire OX13 6BB (GB).

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(54) Title: TRIAZINE DERIVATIVE AS DISPERSANT FOR LUBRICANTS AND FUELS
(57) Abstract

A process for the preparation of a triazine derivative, the reaction products of said process, lubricating oil compositions, fuel compositions and additive concentrates containing such reaction products, and use of the reaction products as dispersant additive.
The present invention relates to triazine derivatives, a process for their preparation, lubricating oil compositions, fuel compositions and additive concentrates containing them and their use as dispersant additives.

In accordance with the present invention there is provided a process for the preparation of a triazine derivative which comprises:

(i) (a) reacting a compound of the formula

\[
\begin{array}{c}
\text{R} \quad \text{N} \\
\text{N} \\
\text{R} \\
\text{R}
\end{array}
\]

(I)

with a polyamine (II) containing at least two -NH\(_2\) and/or -NH groups and (b) reacting the product of (a) with a polyalkeny1 derivative of an ethylenically unsaturated carboxylic reagent and/or a chlorinated polyalkeny1 derivative;

or

(ii) (a) reacting a compound of formula (I) with a lipophilic amine, (b) reacting the product of (a) with a polyamine (II), and (c) reacting the product of (b) with a polyalkeny1 derivative of an ethylenically unsaturated carboxylic reagent and/or a chlorinated polyalkeny1 derivative;

or

(iii) (a) reacting a compound of formula (I) with a preformed reaction product of a polyalkeny1 derivative of an ethylenically unsaturated carboxylic reagent and a polyamine (II), and (b) optionally reacting the product
of (a) with a polyamine (II) which may be the same as or different from the polyamine (II) used to form said pre-formed reaction product, or with a lipophilic amine, wherein each R, which may be the same or different from one another, is a chlorine atom, an amino or hydroxyl group, or a group selected from

\(-\text{OSO}_2\text{R}, \text{-OSO}_2\text{R}^2, \text{and -COO(CH}_2\text{)}_n\text{C}R^4\text{R}^5,\)

wherein \(R^1\) is an alkyl group; \(R^2\) is a hydrogen atom or an alkyl group; \(R^3, R^4\) and \(R^5\), which may be the same as or different from one another, is each a hydrogen atom or an alkyl group; and \(n\) is 0 or 1; or

(iv) reacting a compound of formula (I), in which each R, which may be the same as or different from one another, is an amino or hydroxyl group, with a polyalkenyl derivative of an ethylenically unsaturated carboxylic reagent or with a polyalkenyl derivative of a polyamine (II), with the proviso that in reaction (iii) (a) when each R is a chlorine atom or one R is an amino group and the others are chlorine atoms, the polyamine (II) used to form said pre-formed reaction product is not diethylene triamine or tetraethylene pentamine, unless step (iii) (b) is carried out.

In the compound of formula (I), each R is preferably a chlorine atom, an amino or hydroxyl group, or a group selected from \(-\text{OSO}_2\text{CH}_3\) and \(-\text{OSO}_2\text{-CH}_3\). Said compounds may be prepared by methods known in the art. Especially preferred examples of the compound of formula (I) are melamine, cyanuric chloride and cyanuric acid.
The polyamine (II) contains at least two -NH₂ and/or -NH groups, the groups each having at least one active hydrogen thereon. Examples of polyamines useful in the present invention are those described in the text from page 16, line 21 to page 19, line 53 of EP-B-0287569.

Preferably the polyamine is a compound of the general formula

\[ H₂N-(CHR₁)ₓ-CH₂-\{A-CH₂-(CHR₁)y\}₂y-NH₂ \]  (III)

wherein A is -NH or -O-, each R¹ independently represents a hydrogen atom or a methyl group, x is in the range 1 to 3, and y is in the range 1 to 10 when A is -NH or y is in the range 1 to 200 when A is -O-. y may also be 0.

In formula (III) above, it is preferred that when A is -NH, then x is 1, each R¹ represents a hydrogen atom, and y is in the range 1 to 8; or when A is -O-, then x is 1, each R¹ represents a methyl group and y is in the range 1 to 50.

Preferred polyamines are polyethylene polyamines and polypropylene polyamines, particularly ethylene diamine (EDA), diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), pentaethylene hexamine (PEHA) and hexaethylene heptamine (HEHA). Especially preferred are EDA and DETA.

The ethylenically unsaturated carboxylic reagent contains a total of at least 3 carbon atoms, preferably a total of from 3 to 50, more preferably from 3 to 30, still more preferably from 4 to 20, and even more preferably from 4 to 10, carbon atoms.

The ethylenically unsaturated carboxylic reagent may be an alpha-beta olefinic unsaturated carboxylic reagent as described at page 6, lines 15 to 48 of EP-B-0285609 or page 6, lines 11 to 39 of EP-B-0287569, e.g. acrylic acid (C₃), methacrylic acid (C₄), cinnamic acid (C₉), crotonic acid (C₄), 2-phenylpropenoic acid (C₉), maleic acid (C₄),
fumaric acid (C₄), glutaric acid (C₅), mesaconic acid (C₅), itaconic acid (methylene succinic acid) (C₅), citraconic acid (methyl maleic acid) (C₅) and functional derivatives thereof such as anhydrides (e.g. maleic anhydride (C₄), glutaric anhydride (C₅), itaconic anhydride (C₅), citraconic anhydride (C₅)), esters (e.g. methyl acrylate (C₄)), amides, imides, salts, acyl halides and nitriles.

Preferably the ethylenically unsaturated carboxylic reagent is selected from monoethylenically unsaturated C₄-C₁₀ dicarboxylic acids and anhydrides, of which maleic anhydride is most preferred.

The polyalkenyl derivative of an ethylenically unsaturated carboxylic reagent may be prepared by methods known in the art. For example, if the ethylenically unsaturated carboxylic reagent is maleic anhydride, the polyalkenyl derivative thereof may conveniently be prepared by mixing a polyalkene with a specified amount of maleic anhydride and passing chlorine through the mixture, e.g. as described in GB-A-949981. Alternatively, the derivative may be prepared by reacting thermally, at an appropriate temperature, the polyalkene with a specified amount of maleic anhydride, e.g. as described in GB-A-1483729. In EP-A-0542380 is described a process for preparing such a derivative, which involves reacting the polyalkene with maleic anhydride in a mol ratio of maleic anhydride to polyalkene of greater than 1:1, at a temperature in the range from 150 to 260°C and in the presence of a polyaddition-inhibiting amount of a sulphonic acid. The molar ratio of ethylenically unsaturated carboxylic moiety to polyalkenyl moiety in the derivative formed is preferably 1:1 to 5:1, more preferably 1:1 to 3.5:1, particularly 1.5:1 to 1.2:1.
The chlorinated polyalkenyl derivative may also be prepared by methods known in the art, e.g. by passing chlorine into the polyalkene.

The polyalkene used to prepare the polyalkene derivative may be a homopolymer or copolymer, for example of at least one C$_2$-10 monoolefin. Preferably the polyalkene is a polymer of at least one C$_2$-5 monoolefin, e.g. an ethylene-propylene copolymer. The monoolefin is preferably a C$_3$-4 olefin, in particular propylene or isobutylene, and preferred polyalkenes derived therefrom include polyisobutylene and atactic or isotactic or syndiotactic propylene oligomers. Polyisobutylenes such as that sold by BASF under the trade mark "GLISSOPAL" and those sold by the British Petroleum Company under the trade marks "ULTRAVIS" (both having high levels (about 80 to 90%) of terminal vinylidene unsaturation), "HYVIS" and "NAPVIS", e.g. "HYVIS 75", "HYVIS 120", "NAPVIS 10", "HYVIS 200" and "NAPVIS 120" polyisobutylenes, are especially preferred for use in the present invention.

The polyalkene has a number average molecular weight ($M_n$) preferably in the range from 300 to 7000, more preferably from 500 to 5000, still more preferably from 700 to 3000.

The lipophilic amines used in the present invention may be straight chain, branched, saturated or unsaturated, and include aromatic amines. Especially preferred are dodecylamine (C$_{12}$), dioctylamine (C$_{16}$) and oleylamine (C$_{18}$). A tertiary C$_{18}$ primary amine sold as "PRIMENE" JMT (ex. Rohm and Haas) can alternatively be used.

Reactions (i)(a) and (ii)(b) are preferably carried out at a temperature in the range 30 to 200°C, more preferably 40 to 180°C, particularly 50 to 170°C. Said reactions are carried out in the presence of a solvent.
Furthermore, in said reactions, preferably a molar excess of the polyamine (II) over the compound of formula (I) is used, particularly a molar ratio of 2:1 to 20:1, more particularly 5:1 to 16:1, especially 9:1 to 16:1.

Reaction (ii)(a) is preferably carried out at a temperature in the range 0 to 10°C, preferably 0 to 5°C. Said reaction may be carried out in the presence of a solvent, and in the presence of a base such as sodium carbonate or sodium bicarbonate. The product of said reaction may be subjected to an aqueous wash.

Suitable solvents include hydrocarbon solvents such as higher alkanes, toluene, xylene, mesitylene, e.g. "SHELL SOL" (trade mark) A solvent available from member companies of the Royal Dutch/Shell Group of Companies; also synthetic and mineral oils such as "HVI-60"; ether solvents such as tetrahydrofuran and 1,4-dioxane; nitriles such as acetonitrile; alcohols such as 1-pentanol (amyl alcohol) and 2-methyl-2-propanol (tert-butyl alcohol); and chlorohydrocarbons such as 1,1,1-trichloroethane. The process may be carried out in the absence of a solvent but, as indicated above, is conveniently carried out in the presence of one. Any water or excess of alcohol may be removed using for example a Dean and Stark trap.

Reactions (i)(b) and (ii)(c) are preferably carried out at a temperature in the range 140 to 230°C, more preferably 150 to 210°C. They are also preferably carried out in the presence of an inert gas, for example a nitrogen stream.

The molar ratio of the products of reactions (i)(a) and (ii)(b): polyalkenyl derivative of an ethylenically unsaturated carboxylic reagent is preferably in the range 1:1 to 10:1, more preferably 1:1 to 5:1, particularly 1:1 to 2.5:1.
Reaction (iii)(a) is preferably carried out at a temperature in the range 120 to 280°C, more preferably 140 to 240°C.

Reaction (iii)(b) is preferably carried out at a temperature in the range 120 to 280°C, more preferably 140 to 240°C.

Reaction (iv) is preferably carried out at a temperature in the range 25 to 280°C, more preferably 100 to 240°C.

In the process of the present invention, the molar ratio of lipophilic amine:compound of formula (I) is preferably 1:1 to 10:1, more preferably 1:1 to 5:1, particularly 1:1 to 2:1.

The pre-formed reaction product of a polyalkenyl derivative of an ethylenically unsaturated carboxylic reagent and a polyamine (II) may be prepared according to techniques conventional in the art. Thus, for example, if the ethylenically unsaturated carboxylic reagent is maleic anhydride and the polyamine is ethylene polyamine, they may conveniently be reacted together in a molar ratio of polyalkenyl derivative to polyamine from 1:1 to 4:1, in a hydrocarbon solvent at a temperature in the range from 100 to 250°C, e.g. as described in EP-A-0587250. The molar coupling ratio of polyalkenyl derivative to amine in the product is preferably in the range 1:1 to 3:1, more preferably 1:1 to 2.5:1.

The molar ratio (polyalkenyl derivative of an ethylenically unsaturated carboxylic reagent):(polyamine) for the reactants of the present invention is preferably in the range from 1:1 to 4:1, more preferably from 1:1 to 3:1, most preferably from 1:1 to 2.5:1.

The present invention further provides the reaction product of the above-described process according to the present invention.
The reaction product of the present invention may be used as an additive in lubricating oils. Accordingly, the present invention provides a lubricating oil composition comprising a major amount (more than 50%w) of a lubricating base oil and a minor amount (less than 50%w), preferably from 0.1 to 20%w, especially from 0.5 to 10%w (active matter), of a reaction product according to the present invention, the percentages by weight being based on the total weight of the composition.

A lubricant formulation may be produced by addition of an additive package to the lubricating oil. A minor amount of viscosity modifier may be included if the final lubricant formulation is to be a multigrade version. The type and amount of additive package used in the formulation depends on the final application, which can include spark-ignition and compression-ignition internal combustion engines, including automobile and truck engines, marine and railroad diesel engines, gas engines, stationary power engines and turbines.

The lubricant formulation is blended to meet a series of performance specifications as classified in the US by a tripartite arrangement between the Society of Automotive Engineers (SAE), American Petroleum Institute (API) and American Society for Testing and Materials (ASTM). Also the American Automobile Manufacturers Association (AAMA) and Japan Automobile Manufacturers Association Inc. (JAMA), via an organisation called the International Lubricant Standardisation and Approval Committee (ILSAC), jointly develop minimum performance standards for gasoline-fuelled passenger car engine oils.

In Europe, engine oil classifications are set by the Association des Constructeurs Europeens de l'Automobile (ACEA) in consultation with the Technical Committee of Petroleum Additive Manufacturers (ATC) and Association
Technique de l'Industries Europeens des Lubrifiants (ATIEL). Besides these internationally recognised oil classification systems, many, if not all, Original Equipment Manufacturers (OEMs) have their own in-house performance requirements that must be met by lubricant formulations used for first (i.e. factory) fill.

Suitable lubricating base oils are natural, mineral or synthetic lubricating oils.

Natural lubricating oils include animal and vegetable oils, such as castor oil. Mineral oils comprise the lubricating oil fractions derived from crude oils, e.g. of the naphthenic or paraffinic types or mixtures thereof, coal or shale, which fractions may have been subjected to certain treatments such as clay-acid, solvent or hydrogenation treatments. Synthetic lubricating oils include synthetic polymers of hydrocarbons, e.g. derived from polyalphaolefins, isomerised slack wax, modified alkylene oxide polymers and esters, which are known in the art. These lubricating oils are preferably crankcase lubricating oil formulations for spark-ignition and compression-ignition engines, but include also hydraulic lubricants, metal-working fluids and automatic transmission fluids.

Preferably the lubricating base oil component of the compositions according to the present invention is a mineral lubricating oil or a mixture of mineral lubricating oils, such as those sold by member companies of the Royal Dutch/Shell Group of Companies under the designations "HVI", or the synthetic hydrocarbon base oils sold by member companies of the Royal Dutch/Shell Group of Companies under the designation "XHVI" (trademark).

The viscosity of the lubricating base oils present in the compositions according to the present invention may
vary within wide ranges, and is generally from 3 to 35 mm²/s at 100°C.

The lubricating oil compositions according to the present invention may contain various other additives known in the art, such as:

(a) Viscosity index improvers or modifiers. The viscosity modifier may be of the solid type or a concentrate in a natural or synthetic base stock and can be defined as a substance, usually a polymer, which substantially improves (e.g. by at least 5 units) the viscosity index (e.g. as determined by ASTM procedure D2270) by its incorporation. These can all be incorporated into the final lubricant formulation to give the desired performance properties thereof. Examples of such viscosity modifiers are linear or star-shaped polymers of a diene such as isoprene or butadiene, or a copolymer of such a diene with optionally substituted styrene. These copolymers are suitably block copolymers and are preferably hydrogenated to such an extent as to saturate most of the olefinic unsaturation. A number of other types of viscosity modifier are known in the art, and many of these are described in Proceedings of Conference "Viscosity and flow properties of multigrade engine oils", Esslingen, Germany, December 1977. It is also known in the art that viscosity modifiers can be functionalised to incorporate dispersancy (e.g. dispersant viscosity index improvers based on block copolymers, or polymethacrylates) and/or antioxidant functionality as well as viscosity modification and they can also have pour point depressants mixed in to give handleable products in cold climates.
(b) Ashless or ash-containing extreme pressure/anti-wear additives, such as, for example, those of the metal containing dithiophosphate or ashless dithiocarbamate type, and mixtures thereof. The actual composition of the individual components will vary depending upon final application and hence can be based on a range of metal ion types and various alcohols, in which both alkyl and aryl moieties may be of varying size. Preferred are zinc dithiophosphates (ZDTPs) or sodium dithiophosphates.

(c) Dispersants including succinimides and Mannich bases, both of various molecular weights and amine type, including borated versions, or esters also of varying type and molecular weight. Preferred are ashless dispersants such as polyolefin-substituted succinimides, e.g. those described in GB-A-2231873.

(d) Anti-oxidants, for example of the aminic type such as “IRGANOX” (trade mark) L57 (tertiary C₄-C₁₂ alkyl diphenylamine) or phenolic type such as “IRGANOX” (trade mark) L135 (2,6-ditertiary-butyl-4-(2-carboxy(alkyl)ethyl)phenol) (ex. CIBA Speciality Chemicals) or a soluble copper compound at a copper concentration of between 50 and 500 ppm.

(e) Anti-rust compounds of, for example, the ethylene/propylene block copolymer type.

(f) Friction modifiers for fuel economy, either metal (e.g. molybdenum) containing, or metal free esters and amines, or synergistic mixtures thereof.

(g) Metal containing detergents such as phenates, sulphonates, salicylates or naphthenates, or mixtures thereof, all of which detergents may be either neutral or overbased, such overbased detergents being carbonates, hydroxides or mixtures thereof. The metals are preferably calcium, magnesium or
manganese, although alkali metals such as sodium or potassium could also be used. (h) Copper passivators, preferably of the alkylated or benzylated triazole type.

The reaction product of the present invention may also be used as an additive in fuels. Accordingly, the present invention further provides a fuel composition comprising a major amount (more than 50% w) of a base fuel and a minor amount (less than 50% w), preferably from 0.001 to 2% w, more preferably from 0.001 to 0.5% w and especially from 0.002 to 0.2% w (active matter), of a reaction product according to the present invention, the percentages by weight being based on the total weight of the composition.

Suitable base fuels include gasoline and diesel fuel. These base fuels may comprise mixtures of saturated, olefinic and aromatic hydrocarbons, and may contain a range of sulphur levels, e.g. in the range 0.001 to 0.1% w. They can be derived from straight-run gasoline, synthetically produced aromatic hydrocarbon mixtures, thermally catalytically cracked hydrocarbon feedstocks, hydrocracked petroleum fractions or catalytically reformed hydrocarbons.

The fuel compositions according to the present invention may contain various other additives known in the art, such as:

(a) Anti-knock additives, such as lead compounds, or other compounds such as methyl cyclopentadienyl-manganese tricarbonyl or orthoazidophenyl.

(b) Co-antiknock additives, such as benzoylacetone.

(c) Dehazers, such as those commercially available as "NALCO" (trade mark) EC5462A (ex. Nalco), "TOLAD" (trade mark) 2683 (ex. Baker Petrolite), EXP177, EXP159M, EXP175, EP409 or EP435 (ex. RE Speciality
Chemicals), and T9360-K, T9305, T9308, T9311 or T327 (ex. Baker Petrolite).

(d) Anti-foaming agents, such as those commercially available as "TEGOPREN" (trade mark) 5851, Q 25907, MR1027, MR2068 or MR2057 (ex. Dow Corning), "RHODORSIL" (trade mark) (ex. Rhone Poulenc), and "WITCO" (trade mark) SAG TP325 or SAG327 (ex. Witco).

(e) Ignition improvers (e.g. 2-ethylhexyl nitrate, cyclohexyl nitrate, di-tertiary-butyl peroxide and those disclosed in US-A-4208190 at Column 2, line 27 to Column 3, line 21)

(f) Anti-rust agents (e.g. that commercially sold by Rhein Chemie, Mannheim, Germany as "RC 4801", or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms (e.g. the pentaerythritol diester of polyisobutylene-substituted succinic acid)

(g) Reodorants.

(h) Anti-wear additives.

(i) Anti-oxidants (e.g. phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine).

(j) Metal deactivators.

(k) Lubricity agents, such as those commercially available as EC831, "PARADYNE" (trade mark) 631 or 655 (ex. Paramins) or "VEKTRON" (trade mark) 6010 (ex. Shell Additives International Limited).

(l) Carrier fluids such as a polyether e.g. a C_{12}-C_{15} alkyl-substituted propylene glycol ("SAP 949"), "HVI" or "XHVI" (trade mark) base oil, which are commercially available from member companies of the Royal Dutch/Shell Group of Companies, a polyolefin
derived from C₂-C₆ monomers, e.g. polyisobutylene having from 20 to 175, particularly 35 to 150, carbon atoms, or a polyalphaolefin having a viscosity at 100°C in the range 2 x 10⁻⁶ to 2 x 10⁻⁵ m²/s (2 to 20 centistokes), being a hydrogenated oligomer containing 18 to 80 carbon atoms derived from at least one alphaolefinic monomer containing from 8 to 18 carbon atoms.

The lubricating oil and fuel compositions of the present invention may be prepared by adding the reaction product of the present invention to a lubricating base oil or base fuel. Conveniently, an additive concentrate is blended with the lubricating base oil or base fuel. Such a concentrate generally comprises an inert carrier fluid and one or more additives in a concentrated form. Hence the present invention also provides an additive concentrate comprising an inert carrier fluid and from 10 to 80%w (active matter) of a reaction product according to the present invention, the percentages by weight being based on the total weight of the concentrate.

Examples of inert carrier fluids include hydrocarbons and mixtures of hydrocarbons with alcohols or ethers, such as methanol, ethanol, propanol, 2-butoxyethanol or methyl tert-butyl ether. For example, the carrier fluid may be an aromatic hydrocarbon solvent such as toluene, xylene, mixtures thereof or mixtures of toluene or xylene with an alcohol. Alternatively, the carrier fluid may be a mineral base oil or mixture of mineral base oils, such as those sold by member companies of the Royal Dutch/Shell Group of Companies under the designations "HVI", e.g. "HVI 60" base oil, or the synthetic hydrocarbon base oils sold by member companies of the Royal Dutch/Shell Group of Companies under the designation "XHVI" (trade mark).
Non-limiting examples of suitable additive concentrations in final blended lubricating oil compositions are:

<table>
<thead>
<tr>
<th>Oil component &amp; mass</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
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</thead>
<tbody>
<tr>
<td>Alkaline earth sulphonate detergent</td>
<td>3.8</td>
<td>3.4</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<tr>
<td>Alkaline earth phenate detergent</td>
<td>1.2</td>
<td>1.1</td>
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<tr>
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<td>--</td>
<td>4.6</td>
<td>2.5</td>
<td>3.6</td>
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<td>--</td>
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<td>--</td>
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<td>--</td>
<td>0.6</td>
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<td>0.8</td>
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<td>Phenolic antioxidant</td>
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- 15-
Non-limiting examples of suitable additive concentrates for blending lubricating oil compositions are:

<table>
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<tr>
<th>Oil component % mass</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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<td>Alkaline earth sulphonate detergent</td>
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<td>23.8</td>
<td></td>
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<td>Alkaline earth salicylate detergent</td>
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</tr>
<tr>
<td>High molecular weight dispersant</td>
<td>--</td>
<td>--</td>
<td>38.5</td>
<td>56.3</td>
<td>53.2</td>
<td>68.9</td>
</tr>
<tr>
<td>Low molecular weight dispersant</td>
<td>47.2</td>
<td>14.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>43.1</td>
</tr>
<tr>
<td>Primary ZDTP</td>
<td>3.9</td>
<td>--</td>
<td>--</td>
<td>3.2</td>
<td>--</td>
<td>3.3</td>
</tr>
<tr>
<td>Secondary ZDTP</td>
<td>3.1</td>
<td>7.0</td>
<td>6.3</td>
<td>7.4</td>
<td>7.2</td>
<td>2.9</td>
</tr>
<tr>
<td>Aminic antioxidant</td>
<td>--</td>
<td>--</td>
<td>4.2</td>
<td>8.5</td>
<td>1.8</td>
<td>--</td>
</tr>
<tr>
<td>Phenolic antioxidant</td>
<td>5.5</td>
<td>8.4</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Base oil</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
</tbody>
</table>
The present invention still further provides the use of a reaction product according to the present invention as a dispersant additive.

The present invention will now be further described by reference to the following Examples. In these Examples, the number average molecular weight ($M_n$) specified for the polyisobutene moiety in the polyisobutene succinic anhydride (PIBSA) was determined by gel chromatography using polystyrene standards, e.g. as described in W.W. Yau, J.J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 21979.

Examples 1 to 4 describe the steps of reaction (ii).

**Example 1**

(a) Cyanuric chloride (0.01 mol) in toluene was reacted at 5°C with the lipophilic amine dodecylamine (0.01 mol) in the presence of aqueous sodium bicarbonate (0.02 mol). Following an aqueous wash, the mixture was stripped to give the crude desired 6-dodecylamino-2,4-dichloro-1,3,5-triazine ("alkylaminocyanuric chloride") in 99% isolated yield.

(b) DETA was then reacted with the alkylaminocyanuric chloride from step (a) (molar ratio 10:1) at a temperature of 60°C. The product was isolated by toluene/water partition, giving a 82% yield.

(c) The product from step (b), in toluene, was added to a low molecular weight PIBSA (PIB $M_n$ about 950). Toluene was distilled out and heating continued under a stream of nitrogen for 6 to 7 hours at 160°C.

**Example 2**
The steps described in Example 1 were followed except that in step (c) a high molecular weight PIBSA (PIB Mn about 2270) was used.

Example 3

The steps described in Example 1 were followed except that in step (a) dioctylamine was used as the lipophilic amine.

Example 4

The steps described in Example 2 were followed except that in step (a) dioctylamine was used as the lipophilic amine.

Examples 5 to 17

Further compounds were prepared, the characteristics of all the Examples being set out in Table 1:
Table 1

<table>
<thead>
<tr>
<th>Example</th>
<th>Lipophilic amine</th>
<th>Polyamine</th>
<th>Mn of PIB in PIBSA</th>
<th>Coupling ratio PIBSA: polyamine</th>
<th>Step (c) reaction temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>dodecylamine</td>
<td>DETA</td>
<td>~950</td>
<td>2.0</td>
<td>160</td>
</tr>
<tr>
<td>2</td>
<td>dodecylamine</td>
<td>DETA</td>
<td>~2270</td>
<td>2.0</td>
<td>160</td>
</tr>
<tr>
<td>3</td>
<td>dioctylamine</td>
<td>DETA</td>
<td>~950</td>
<td>2.0</td>
<td>160</td>
</tr>
<tr>
<td>4</td>
<td>dioctylamine</td>
<td>DETA</td>
<td>~2270</td>
<td>2.0</td>
<td>160</td>
</tr>
<tr>
<td>5</td>
<td>oleylamine</td>
<td>EDA</td>
<td>~950</td>
<td>1.5</td>
<td>200</td>
</tr>
<tr>
<td>6</td>
<td>oleylamine</td>
<td>EDA</td>
<td>~950</td>
<td>2.0</td>
<td>200</td>
</tr>
<tr>
<td>7</td>
<td>oleylamine</td>
<td>EDA</td>
<td>~2270</td>
<td>1.5</td>
<td>200</td>
</tr>
<tr>
<td>8</td>
<td>oleylamine</td>
<td>EDA</td>
<td>~2270</td>
<td>2.0</td>
<td>200</td>
</tr>
<tr>
<td>9</td>
<td>oleylamine</td>
<td>EDA</td>
<td>~950</td>
<td>2.0</td>
<td>160</td>
</tr>
<tr>
<td>10</td>
<td>oleylamine</td>
<td>EDA</td>
<td>~2270</td>
<td>2.0</td>
<td>160</td>
</tr>
<tr>
<td>11</td>
<td>oleylamine</td>
<td>EDA</td>
<td>~950</td>
<td>1.5</td>
<td>160</td>
</tr>
<tr>
<td>12</td>
<td>&quot;PRIMENE&quot;</td>
<td>EDA</td>
<td>~950</td>
<td>1.5</td>
<td>200</td>
</tr>
<tr>
<td>13</td>
<td>&quot;PRIMENE&quot;</td>
<td>EDA</td>
<td>~2270</td>
<td>1.5</td>
<td>200</td>
</tr>
<tr>
<td>14</td>
<td>oleylamine</td>
<td>DETA</td>
<td>~950</td>
<td>1.5</td>
<td>200</td>
</tr>
<tr>
<td>15</td>
<td>oleylamine</td>
<td>DETA</td>
<td>~2270</td>
<td>1.5</td>
<td>200</td>
</tr>
<tr>
<td>16</td>
<td>oleylamine</td>
<td>DETA</td>
<td>~950</td>
<td>2.0</td>
<td>200</td>
</tr>
<tr>
<td>17</td>
<td>oleylamine</td>
<td>DETA</td>
<td>~2270</td>
<td>2.0</td>
<td>200</td>
</tr>
</tbody>
</table>

Example 18

Carbon Black Dispersancy Test (CBDT)
(British Rail Publication BR 669:1984)

Samples of a SAE 15W40 Middle East lubricating oil containing a commercial package of a zinc dialkyldithiophosphate, an overbased calcium alkyl salicylate and VI improver, were modified by incorporation of the reaction products of Examples 1 to 4 to give oils containing said products at a concentration of 1%w active matter. 3%w of carbon black
was then added to each oil and (percentage) increase in kinematic viscosity at 60°C was determined, using an Ubbelohde viscometer. A low result indicates good performance. The absolute values obtained are dependent on the active surface area of the carbon black used, and therefore comparative series should be tested with identical samples of carbon black. The tests were carried out using "Flamrus" (trade mark) carbon black.

The results of this test are given in Table 2:

<table>
<thead>
<tr>
<th>Example</th>
<th>% viscosity increase*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
</tr>
</tbody>
</table>

* relative to viscosity of dispersant blend without carbon black

Example 19
Rheology Test

This test used the Haake RV20 Rotary Viscometer and comprised adding a known concentration (2%w active matter) of the dispersant under test to a mixture of other compounds, to produce a fully formulated oil. Carbon black was then added to result in a content of 4.76%w in the oil and mixed at an elevated temperature (90°C) for a set period of time (at least 6 hours). The viscometric characteristics of the oils containing Examples 5 and 14 were then measured and compared under the same conditions, together with the commercial products "SAP 286" and "SAP 230TP" (mono/bis PIB succinimides, ex Shell Additives International Limited).

The base oil blends used in the Haake rheology test
consisted of the following components:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration % w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detergents (overbased calcium and magnesium alkyl salicylates)</td>
<td>3.5</td>
</tr>
<tr>
<td>Anti-wear additive (zinc dithiophosphate(ZDTP))</td>
<td>1.13</td>
</tr>
<tr>
<td>Viscosity index improver (hydrogenated polyisoprene)</td>
<td>5.88</td>
</tr>
<tr>
<td>Pour point depressant (polymethacrylate)</td>
<td>0.34</td>
</tr>
<tr>
<td>Mixture of base oils</td>
<td>89.15</td>
</tr>
</tbody>
</table>

The Haake rheology test apparatus comprises a Haake RV 20 rheometer with RC 20 rheocontroller and CV 100 measuring system with a ZA 30 cup and rotor.

The samples were prepared by weighing (100/active matter)g of the dispersant sample, made up to 5.75 g with HVI-60-AL base oil, and then 50 g total mass with the base oil blend.

The carbon black (grade XC72) was activated at 140°C for at least 12 hours prior to use in the rheology test. An amount, 0.25 to 0.30 g, of the carbon black was measured, and fully formulated oil was added in an amount as calculated by the formula:

\[ M_{FFO} = M_C \times 20 \]

where \( M_{FFO} \) is the mass of the fully formulated oil (g), and \( M_C \) is the mass of carbon black (g). The mixture was completely homogenised with the oil. The viscosity characteristics were measured after at least 6 hours at 90°C over a range of shear rates for 30 minutes, as shown in Figure 1.
From Figure 1, it can be seen that Examples 5 and 14 exhibit improved dispersancy as compared to "SAP 286" and "SAP 230TP".

Example 20

5 Fluorooelastomer Seals Test

Reaction products of the present invention are less aggressive to fluorooelastomer seals, as demonstrated in the Mercedes-Benz fluorooelastomer seals test. When seal fluorooelastomer was subjected to a formulation containing Example 5 its tensile strength was reduced by 13.3% and the extent to which it could be stretched before breaking was reduced by only 17.6%; the figures for analogous formulations, at the same dispersant treat rate (13.5%w), containing, instead, "SAP 286" and "SAP 230TP", are shown in Table 3:
Example 21

Corrosion Test

Reaction products of the present invention display reduced corrosion, as demonstrated in the L-10 bench corrosion test without severity adjustment (ref. API CG-4 test). The results, at the same dispersant treat rates (13.5%w), are shown in Table 4, from which the improved performance of Example 5 as compared to "SAP 286" and "SAP 230TP" is apparent:

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength change %</th>
<th>Elongation change %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 5</td>
<td>-13.3</td>
<td>-17.6</td>
</tr>
<tr>
<td>SAP 286</td>
<td>-52.1</td>
<td>-52.5</td>
</tr>
<tr>
<td>SAP 230TP</td>
<td>-51.9</td>
<td>-57.1</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal content of the oil after test (ppm)</th>
<th>Copper</th>
<th>Lead</th>
<th>Tin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 5</td>
<td></td>
<td>3</td>
<td>9</td>
<td>&lt;1</td>
</tr>
<tr>
<td>SAP 286</td>
<td></td>
<td>9</td>
<td>86</td>
<td>1</td>
</tr>
<tr>
<td>SAP 230TP</td>
<td></td>
<td>12</td>
<td>206</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
1. A process for the preparation of a triazine derivative which comprises:

(i) (a) reacting a compound of the formula

\[
\begin{array}{c}
\text{R} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{R} \\
\end{array}
\]

(I)

with a polyamine (II) containing at least two \(-\text{NH}_2\) and/or \(-\text{NH}\) groups and (b) reacting the product of (a) with a polyalkenyl derivative of an ethylenically unsaturated carboxylic reagent and/or a chlorinated polyalkenyl derivative;

or

(ii) (a) reacting a compound of formula (I) with a lipophilic amine, (b) reacting the product of (a) with a polyamine (II), and (c) reacting the product of (b) with a polyalkenyl derivative of an ethylenically unsaturated carboxylic reagent and/or a chlorinated polyalkenyl derivative;

or

(iii) (a) reacting a compound of formula (I) with a preformed reaction product of a polyalkenyl derivative of an ethylenically unsaturated carboxylic reagent and a polyamine (II), and (b) optionally reacting the product of (a) with a polyamine (II) which may be the same as or different from the polyamine (II) used to form said preformed reaction product, or with a lipophilic amine,
wherein each R, which may be the same or different from one another, is a chlorine atom, an amino or hydroxyl group, or a group selected from

\[-\text{OSO}_2R^1, -\text{OSO}_2\text{R}^2, \quad \text{and} \quad -\text{OCO(CH}_2)_n\text{CR}^3\text{R}^4\text{R}^5,\]

wherein \(R^1\) is an alkyl group; \(R^2\) is a hydrogen atom or an alkyl group; \(R^3, R^4\) and \(R^5\), which may be the same as or different from one another, is each a hydrogen atom or an alkyl group; and \(n\) is 0 or 1; or

(iv) reacting a compound of formula (I), in which each R, which may be the same as or different from one another, is an amino or hydroxyl group, with a polyalkenyl derivative of an ethylenically unsaturated carboxylic reagent or with a polyalkenyl derivative of a polyamine (II),

with the proviso that in reaction (iii)(a) when each R is a chlorine atom or one R is an amino group and the others are chlorine atoms, the polyamine (II) used to form said pre-formed reaction product is not diethylene triamine or tetraethylene pentamine, unless step (iii)(b) is carried out.

2. A process according to Claim 1, wherein each R is a chlorine atom, an amino or hydroxyl group, or a group

selected from \(-\text{OSO}_2\text{CH}_3\) and \(-\text{OSO}_2\text{CH}_3\).

3. A process according to Claim 1 or 2, wherein the polyamine is ethylene diamine or diethylene triamine.

4. A process according to Claim 1, 2 or 3, wherein step (i)(a) is carried out at a temperature in the range 30 to 200°C.
5. A process according to any one of Claims 1 to 4, wherein step (i)(b) is carried out at a temperature in the range 140 to 230°C.

6. A process according to Claim 1, 2 or 3, wherein step (ii)(a) is carried out at a temperature in the range 0 to 10°C.

7. A process according to any one of Claims 1 to 3 and 6, wherein step (ii)(b) is carried out at a temperature in the range 30 to 200°C.

8. A process according to any one of Claims 1 to 3, 6 and 7 wherein step (ii)(c) is carried out at a temperature in the range 140 to 230°C.

9. A process according to Claim 1, 2 or 3, wherein step (iii)(a) is carried out at a temperature in the range 120 to 280°C.

10. A process according to any one of Claims 1 to 3 and 9, wherein step (iii)(b) is carried out at a temperature in the range 120 to 280°C.

11. A process according to Claim 1, 2 or 3, wherein reaction (iv) is carried out at a temperature in the range 25 to 280°C.

12. A process according to any one of the preceding Claims, wherein the ethylenically unsaturated carboxylic reagent is selected from monoethylenically unsaturated C4-10 dicarboxylic acids and anhydrides.

13. A process according to any one of the preceding Claims, wherein the polyalkenyl derivative is derived from a polyalkene which is a polymer of at least one C2-10 monoolefin.

14. A process according to any one of the preceding Claims wherein each R is a chlorine atom.

15. The reaction product of the process according to any one of the preceding Claims.
16. A lubricating oil composition comprising a major amount of a lubricating base oil and a minor amount of a reaction product according to Claim 15.
17. A fuel composition comprising a major amount of a base fuel and a minor amount of a reaction product according to Claim 15.
18. An additive concentrate comprising an inert carrier fluid and from 10 to 80%w, based on the total concentrate, of a reaction product according to Claim 15.
19. Use of a reaction product according to Claim 15 as a dispersant additive.
Fig. 1.

- Example 5
- SAP 230 TP
- Example 14
- SAP 286

Viscosity, Pa·s

Shear rate, s⁻¹