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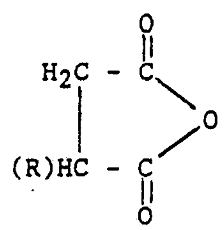
(54) Lubricating oil additives.

(57) A process for the production of a dispersant additive for use in lubricating oil compositions comprises reacting at elevated temperature,

(a) the product (A) of a reaction between a polyamine and a polyalkenyl succinic anhydride of the general formula (I) or the corresponding succinic acid



(I)

where R represents an alkyl or alkenyl group, and

(b) a polycarboxylic acid containing between 30 and 500 carbon atoms. Products of said process can be used in lubricating oil compositions and in additive concentrates for use in lubricating oil compositions.

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LUBRICATING OIL ADDITIVES

The present invention relates generally to additives for use in lubricating oil compositions and in particular to such compositions comprising additives which are dispersants having viscosity index improving properties.

Operation of internal combustion engines is accompanied by the formation of piston varnish and sludge in the crankcase and in the oil passages of the engine. The sludge and varnish seriously restrict the ability of the crankcase oil to satisfactorily lubricate the engine. Furthermore, the sludge with its entrapped water tends to contribute to rust formation in the engine. To combat the varnish and sludge in internal combustion engines it has long been the practice to incorporate into the lubricating oil, additives in the form of dispersants. The dispersants function to disperse the components of varnish and sludge throughout the oil and thereby prevent their accumulation.

It has long been known to use nitrogen-containing compounds as dispersants and/or detergents. Many of the known nitrogen-containing dispersants and/or detergent compounds are based on the reaction of an alkenylsuccinic acid or anhydride with an amine or polyamine to produce an alkenylsuccinimide or an alkenylsuccinamic acid depending upon the nature of the reactants and the reaction conditions. Thus, US Patents Nos. 3,172,892 and 4,048,080 disclose alkenylsuccinimides formed from the reaction of an alkenylsuccinic anhydride and an alkylene polyamine and their use as dispersants in lubricating oil compositions. US Patent No. 2,568,876 discloses reaction products prepared by reacting a monocarboxylic acid with a polyalkylene polyamine followed by a reaction of the intermediate product with an alkenyl succinic anhydride. US Patent No. 3,216,936 discloses a process for preparing an aliphatic lubricant additive which involves reacting an alkylene amine, a polymer-substituted succinic acid and an aliphatic monocarboxylic acid.

More recently, the operating demands placed on internal combustion engines have led to a desirability for the dispersant additive to make a viscosity index improver contribution to the additive package sufficient to permit elimination of all or a significant amount of the viscosity index improver additive conventionally employed in such packages. In this connection GB-A-1565627 claims a lubricating composition comprising a major amount of oil of lubricating viscosity and a minor amount of one or more carboxylic derivatives produced by reacting at least one substituted succinic acylating agent with a reactant selected from (a) an amine having within its structure at least one H-N group, (b) an alcohol, (c) a reactive metal or reactive metal compound, and (d) a combination of two or more of any of (a) to (c), the components of (d) being reacted with said one or more substituted succinic acylating agents simultaneously or sequentially in any order, wherein said substituted succinic acylating agent(s) consist of substituent groups and succinic groups wherein the substituent groups are derived from polyalkene, said polyalkene having a Mn value of 1300 to 5000 and a M_w/M_n value of 1.5 to 4, said acylating agent(s) having within their structure an average of at least 1.3 succinic groups for each equivalent weight (as hereinbefore defined) of substituent groups.

Also claimed in GB-A-1565627 is a process for producing one or more substituted acylating agents by heating at a temperature of at least 140 °C:

(A) Polyalkene having an M_n value of 1300 to 5000 and a M_w/M_n value of 1.5 to 4,

(B) One or more acidic reactants ofthe formula

$$X-\overset{\displaystyle O}{\overset{\|}{C}}-HC=CH-\overset{\displaystyle O}{\overset{\|}{C}}-X^1$$

wherein X and X^1 are the same or different provided at least one of X and X^1 is such that the substituted acylating agent can function as a carboxylic acylating agent, or X and X^1 are joined and form an -O-link,

(C) Chlorine,

wherein the mole ratio of (A):(B) is such that there is at least 1.3 moles of (B) for each of (A) where the number of moles of (A) is the quotient of the total weight of (A) divided by the value of Mn, and the amount of chlorine employed is such as to provide at least 0.2 mole of chlorine for each mole of (B) to be reacted with (A).

It is a consequence of using chlorine in the preparative procedure that the substituted acylating agents and the carboxylic derivatives of GB-A-1565627 can contain residual chlorine, which can be detrimental in lubricating oil applications.

Another approach to the production of dispersant additives capable of making a viscosity index contribution is disclosed in US Patent No. 4,713,191 in which there is disclosed a lubricating oil composition comprising a major portion of a lubricating oil and a minor dispersant amount of a reaction product prepared by the process which comprises:

(a) reacting a polyethylene amine with an alkenyl succinic acid anhydride to form a bis-alkenyl succinimide,

(b) acylating said bis-alkenyl succinimide with glycolic acid to form a partially glycolated bis-alkenyl succinimide,

(c) adding an organic diisocyanate to said glycolated bis-alkenyl succinimide, thereby forming a diurea coupled glycamide bis-alkenyl succinimide, and

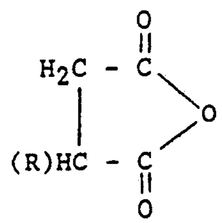
(d) recovering said diurea coupled glycamide bis-alkenyl succinimide.

In the process of USP 4,713,191 the purpose of adding the glycolic acid is to acylate all of the free basic amines except for one or one equivalent amine to form the partially glycolated bis-alkenyl succinimide.

We have now found that dispersants capable of making a viscosity index contribution to the finished lubricating oil can be produced by crosslinking polyalkenyl succinimides by reaction with higher molecular weight di- and poly-carboxylic acids.

Accordingly, the present invention provides a process for the production of a dispersant additive for use in lubricating oil compositions which process comprises reacting at elevated temperature a polyalkenyl succinimide with a di- or poly-carboxylic acid containing sufficient carbon atoms to impart oil solubility to the resulting product.

By polyalkenyl succinimide is understood the product of a reaction between a polyamine and a polyalkenyl succinic anhydride of the general formula (I) or the corresponding succinic acid:-



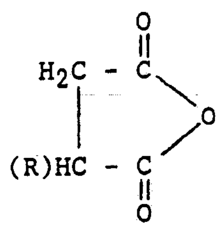
(I)

where R represents an alkyl or alkenyl group.

Polyalkenyl succinimides are well known in the lubricating oil additive field.

Accordingly the present invention provides a process for the production of a dispersant additive for use in lubricating oil compositions which process comprises reacting at elevated temperature,

(a) the product (A) of a reaction between a polyamine and a polyalkenyl succinic anhydride of the general formula (I) or the corresponding succinic acid



(I)

where R represents an alkyl or alkenyl group, and

(b) a polycarboxylic acid containing between 30 and 500 carbon atoms.

In the general formula (I) for the succinic anhydride, the substituent R is a hydrocarbyl group. The substituent R either has no residual unsaturation in which case R represents an alkyl group, or it has residual unsaturation in which case R represents an alkenyl group. The substituent R is generally derived from a polyolefin which is reacted with maleic anhydride to form the substituted succinic anhydride of the general formula (I). The polyolefin may be any polyolefin having residual unsaturation but is preferably a polyisobutene. The substituent R may suitably have a number average molecular weight (M_n) in the range from about 500 to about 3000, preferably from about 1000 to about 1500.

The polyalkenyl succinimide is produced by reacting a succinic anhydride of the general formula (I) or the corresponding acid, preferably the anhydride, with a polyamine. The polyamine can be an alkylene diamine eg ethylene diamine or polyalkylene polyamine. Although any alkylene diamine or polyalkylene polyamine may be reacted with the polyalkenyl succinic anhydride, generally polyalkylene polyamines comprising at least three amine groups are employed. Suitable polyalkylene polyamines are the polyethylene polyamines, for example triethylene tetramine or tetraethylene pentamine.

The polyalkenyl succinimide can be a monosuccinimide or a bis succinimide or a mixture of both. A monosuccinimide comprises a single succinimide ring, a bis succinimide comprises two succinimide rings. A monosuccinimide will generally be the major reaction product when the molar ratio of succinic anhydride or acid to polyamine is 1:1, a bissuccinimide will generally be the major reaction product when the molar ratio is 2:1. However the product of a reaction between a polyamine and a polyalkenyl succinic anhydride or acid will generally comprise a mixture of both mono and bis succinimides, the relative proportions depending upon the molar ratio of the reactants. It is preferred for the purpose of the present invention that a polyalkenyl succinimide containing a major proportion of monosuccinimide is used.

The di- or poly-carboxylic acid must contain sufficient carbon atoms to impart oil solubility to the final product. The acid will contain from 30 to 500 carbon atoms, preferably 35-400, more preferably 50-350. Terminal carboxylic acids, internal carboxylic acids and mixed terminal/internal carboxylic acids may be employed. Terminal carboxylic acids, are preferred. A useful class of terminal di-carboxylic acids is the polybutadiene diacid end-capped materials. Examples of useful materials in this class are Hycar 2000X162 and 2000X165 (commercially available from B.F. Goodrich.)

The reaction is preferably carried out in a high boiling inert solvent, suitably a high boiling hydrocarbon solvent. In view of the intended application of the product, a preferred solvent is a lubricating oil, which may be a natural or synthetic lubricating oil. Suitable lubricating oils include the Solvent Neutral (SN) oils.

The reaction is carried out at elevated temperature, suitably in the range from 50 to 250 °C, preferably from 75 to 200 °C.

In another aspect, the present invention provides a lubricating oil composition comprising a major proportion of a lubricating oil and a minor proportion of the product of the process as hereinbefore described.

In another aspect, the present invention provides a lubricating oil additive concentrate suitable for use in a lubricating oil composition comprising a product produced by the process as hereinbefore described.

Lubricating oils useful in the compositions of the present invention may be any natural or synthetic lubricating oil. An oil used as a reaction solvent can be the same or different to one used in the preparation of the additive composition. Suitable lubricating oils are described for example in the aforesaid GB-A-1565627, to which the reader is referred for further details.

The lubricating oil composition may contain, in addition to the product produced by the process as hereinbefore described, conventional additives, for example one or more of: detergents, anti-wear/extreme pressure additives, ant ioxidants, anti-rust additives and viscosity index improvers. It is an advantage of the present invention, however, that at least some of the viscosity index improver requirements of the lubricating oil composition may be provided by the dispersant additive produced by the process of the present invention.

The invention will now be further illustrated by reference to the following Examples.

Example 1 (According to the Invention)

A PIB succinimide (60 parts) (prepared by reacting an equimolar mixture of tetraethylenepentamine (TEPA) and a polyisobutene succinic anhydride (PIBSA) wherein the polyisobutene substituent is derived from a polyisobutene of M_n 1000) and a diacid end-capped polybutadiene (Hycar 2000X165 ex B.F. Goodrich) (20 parts) were mixed in SN150 oil in an amount such that there was a total of 50% of active components in solution. The mixture was heated to 180 °C and held at this temperature whilst stirring for 4 hours.

After cooling, a sample of the product was dissolved in further SN150 oil in an amount such that its concentration was 5.5% actives by weight. Its viscometric behaviour was examined and the results are given in the following Table.

Example 2 (According to the Invention)

The procedure of Example 1 was repeated except that the PIB-succinimide (60 parts) was obtained by reacting an equimolar mixture of a PIBSA wherein the polyisobutene substituent is derived from a mixture of polyisobutene of M_n 1000 and M_n 2400 and instead of the Hycar 2000X165 diacid end-capped polybutadiene there was used a higher molecular weight material, Hycar 2000X162 (15 parts).

After cooling, a sample of the product was dissolved in further SN150 oil in an amount such that its concentration was 5.5% actives by weight. Its viscometric behaviour was examined and the results are given in the following Table.

Example 3 (According to the Invention)

A PIB succinimide (60 parts) (prepared by reacting an equimolar mixture of tetraethylenepentamine (TEPA) and a polyisobutene succinic anhydride (PIBSA) wherein the polyisobutene substituent is derived from a polyisobutene of M_n 1000) and a trimerized fatty acid (10.5 parts) (Pripol 1040 ex Unichema) were mixed in SN150 oil in an amount such that there was a total of 50% of active components in solution. The mixture was heated to 180 °C and held at this temperature whilst stirring for 4 hours.

After cooling, a sample of the product was dissolved in further SN150 oil in an amount such that its concentration was 7.3% actives by weight. Its viscometric behaviour was examined and the results are given in the following Table.

TABLE

Example	Concn. (% w/w)	Viscosity at 100 °C (cSt)	Viscosity at 40 °C (cSt)	Viscosity at -20 °C (P)	Viscosity Index
1	5.5	8.34	54.3	37	126
2	5.5	8.90	57.5	39	132
3	7.3	7.55	48.64	41	120
CT1*	7.3	7.38	50.7	47	106

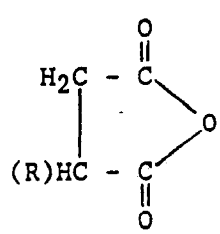
* The material tested in Comparison Test 1 was the starting PIB-succinimide of Example 1.

Improved contribution to VI was noted for products of the invention (Examples 1-3) over conventional succinimide.

Claims

1. A process for the production of a dispersant additive for use in lubricating oil compositions which process comprises reacting at elevated temperature.

(a) the product (A) of a reaction between a polyamine and a polyalkenyl succinic anhydride of the general formula (I) or the corresponding succinic acid



(I)

where R represents an alkyl or alkenyl group, and

(b) a polycarboxylic acid containing between 30 and 500 carbon atoms.

2. A process as claimed in claim 1 wherein the product (A) comprises a major proportion of a monosuccinimide.

3. A process as claimed in either claim 1 or claim 2 wherein R represents an alkyl group or alkenyl group, which group is derived from polyisobutene.

4. A process as claimed in claim 3 wherein said polyisobutene has a number molecular weight in the range 1000 to 1500.

5. A process as claimed in any one of claims 1 to 4 wherein the polyamine comprises at least three amine groups, said amine groups being independently primary or secondary amine groups.

6. A process as claimed in claim 5 wherein said polyamine is either triethylene tetramine or tetraethylene pentamine.

7. A process as claimed in any one of claims 1 to 6 wherein the polycarboxylic acid comprises at least two terminal carboxylic acid groups.

8. A process as claimed in any one of claims 1 to 7 wherein the process is carried out at a temperature in the range 75 - 200 °C.

9. A lubricating oil composition comprising a major proportion of a lubricating oil and a minor proportion of the product of a process as claimed in any one of claims 1 to 8.

10. An additive cencentrate suitable for use in a lubricating oil compostion comprising the product of a process as claimed in any one of claims 1 to 8.

11. A product obtainable by a process as claimed in any one of claims 1 to 8.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 31 2784

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	GB-A-2 140 811 (EXXON RESEARCH AND ENG. CO.) * Page 1, lines 5-42; page 2, lines 1-13; page 3, lines 13-34 * ---	1-6,8-11	C 10 M 133/56 C 10 M 159/12 // (C 10 M 159/12 C 10 M 129:93 C 10 M 133:56 C 10 M 145:16) (C 10 N 30/02 C 10 N 30:04)
X	US-A-3 415 750 (J.F. ANZERBERGER) * Column 1, line 43 - column 3, line 15; column 4, lines 11-16; column 5, lines 1-25; column 7, table I; example 12; column 7, lines 19-28 * ---	1-6,8-11	
A	FR-A-1 430 487 (THE LUBRIZOL CORP.) * Page 2, column 1, line 1 - column 2, line 47; page 3, column 1, line 47 - column 2, line 3; page 4, column 1, line 52 - column 2, line 24 * & US-A-3 216 936 (W.M. LE SUER) (Cat. D) ---	1-6,8-11	
A	US-A-4 548 724 (T.J. KAROL) * Claims 33-39 * ---	1-11	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**
A	GB-A-2 097 800 (EXXON RESEARCH AND ENG. CO.) * Page 3, lines 45-54; page 5, line 46; page 6, lines 12-35,57-61 * ---	1-6,8-11	C 10 M
A	US-A-3 455 827 (E. MEHMEDBASICH) * Claims 1,3,4,5,6 * -----	1-6,8-11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28-02-1990	HILGENGA K.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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