

**LUBRICATING COMPOSITION COMPRISING AN ASHLESS TBN BOOSTER**

The present invention relates in general to lubricating compositions. In particular, embodiments of the invention provide a TBN booster in the form of an amine-containing amphiphilic diblock copolymer, a lubricating composition comprising the same, as well as  
5 a use thereof.

Lubricating compositions generally comprise a base oil of lubricating viscosity together with one or more additives to deliver properties including for example, reduced friction and wear, improved viscosity index, detergency, dispersancy and resistance to oxidation and corrosion by, for example, acidic by-products.

10 Emission standards for gasoline and diesel engines, most recently marine diesel engines, are becoming increasingly stringent, which has necessitated the lowering of the total sulfur, phosphorus and sulfated ash levels of lubricants. However, in order for such Low-“SAPS” (Sulfated Ash, Phosphorus and Sulfur) lubricants to meet performance criteria of industry standards, the lubricants must, *inter alia*, retain their ability to neutralise  
15 acidic by-products from combustion. Historically, lubricants for diesel engines, including two-stroke diesel engines, have generally comprised base in the form of at least one overbased detergent for neutralising acidic by-products. However, overbased detergents contribute significantly to the level of sulfated ash in the composition.

It has been suggested to at least partially replace overbased detergents in a  
20 lubricating composition with ashless, neutral detergents. Although lubricating compositions comprising such neutral detergents may still satisfy detergency requirements, there are significant doubts over whether the total base number (TBN) value of the lubricating composition as well as the  $pK_a$  value, which describes the affinity for interaction with acids, would be high enough to fulfil basicity and other requirements,  
25 particularly in diesel engines. Consequently, there has been increasing focus on providing lubricant additives which can increase the TBN of the lubricant, without contributing to the level of sulfated ash.

WO 2007/117776 describes the use of a succinimide dispersant as an ashless source of TBN in a lubricating composition. WO 2014/074197 discloses a sulfurized aromatic  
30 amine compound as a TBN booster and an antioxidant for a lubricating composition. US 8,143,201 discloses morpholine based compounds useful as ashless TBN sources. Amine-

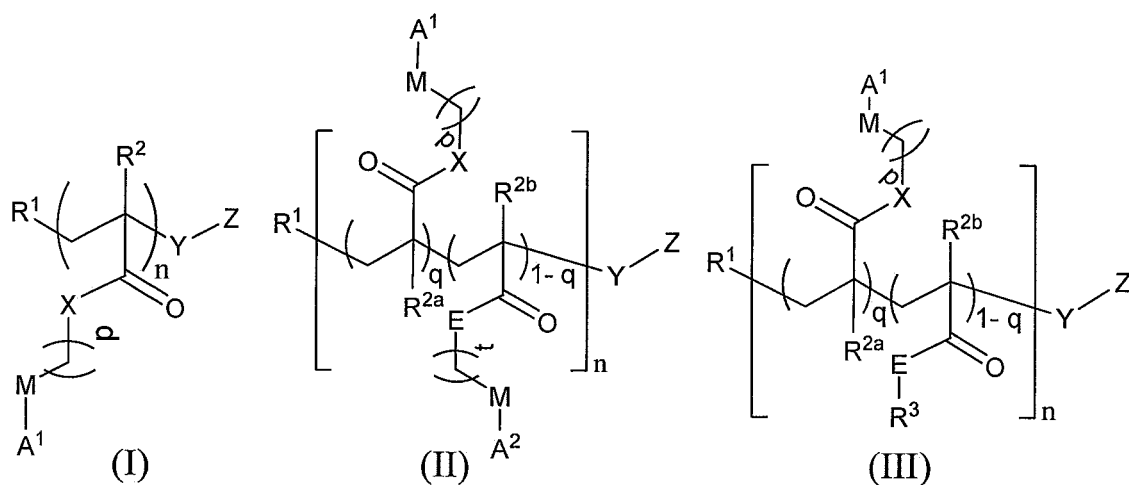
containing TBN boosters that have hitherto been proposed have been known to suffer poor solubility and stability in oil.

Commercial sources of ashless TBN in automotive applications are also primarily derived from dispersants which individually have relatively low BN values (e.g. 14 – 70 mg KOH/g) but which collectively contribute to high level of TBN. However, it is difficult to obtain desirable levels of TBN in this manner whilst also formulating a lubricant at the common viscosity grades (e.g. 0W, 5W, 10W, 20W-20, 30, 40 and 50). For at least these reasons, the use of such TBN boosters in a commercial setting is beset with complications.

There remains a need for alternative ashless TBN boosters which are capable of substantially increasing the TBN of a lubricating composition, thereby minimising the amount of overbased detergents that are required, whilst exhibiting good oil solubility and stability and allowing for the formulation of lubricants at the common viscosity grades.

The present invention is based on the identification of an amine-containing polymer which has properties which make it particularly suitable for use as an ashless TBN booster. Tertiary amine groups on the polymer act as basic groups which are able to neutralise acid and thereby contribute to an increase in the TBN of a lubricant composition in which the polymer is dispersed.

In one aspect, the present disclosure provides a lubricating composition comprising a base oil of lubricating viscosity, one or more lubricant additives and an ashless TBN booster selected from an amine-containing diblock copolymer according to Formula I, II and/or III below:



wherein:

$R^1$  is a  $C_1$  to  $C_{12}$  straight chain or branched alkyl group, a  $C_6$  to  $C_{10}$  aryl group or a 3 to 10 membered heterocyclic group, wherein said alkyl, aryl or heterocyclic groups may be unsubstituted or substituted;

$R^2$ ,  $R^{2a}$  and  $R^{2b}$  are independently H or methyl;

5  $R^3$  is a  $C_1$ - $C_{24}$  straight chain or branched alkyl group;

E is O or NH;

X is O or NH;

Y is S, S(=O), or S(=O)<sub>2</sub>;

Z is selected from:

10  $-\text{CH}_2\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{R}^6$ ,  $\text{CH}_2\text{CH}_2-\text{C}(=\text{O})-\text{R}^6$ ,  $-\text{CH}_2\text{CH}_2-\text{C}(=\text{O})-\text{S}-\text{R}^6$ ,  
 $-\text{CH}_2\text{CH}_2-\text{C}(=\text{O})-\text{NH}-\text{R}^6$ ,  $-\text{CH}_2\text{CH}_2-\text{C}(=\text{S})-\text{NH}-\text{R}^6$ , and  
 $-\text{CH}(-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{R}^6)(-\text{C}(=\text{O})-\text{O}-\text{R}^6)$ ;

$R^6$  is a  $C_6$  to  $C_{50}$  aliphatic hydrocarbyl group;

M is  $\text{CH}_2$ ;

15  $A^1$  and  $A^2$  are independently selected from  $\text{NR}^4\text{R}^5$ , a 3 to 10 membered heterocyclic group containing a nitrogen ring atom which is not attached to M via a nitrogen atom, or a  $C_6$  to  $C_{10}$  aryl group substituted by 1 to 2  $-\text{NR}_j\text{R}_k$  groups; provided that when X and E are the same and  $R^{2a}$  and  $R^{2b}$  are the same,  $A^1$  and  $A^2$  are different;

$R^4$  and  $R^5$  are independently selected from hydrogen, a  $C_1$  to  $C_8$  straight chain or  
 20 branched alkyl group, a  $C_2$  to  $C_8$  straight chain or branched alkenyl group, a  $C_3$  to  $C_8$  cycloalkyl group, a  $C_6$  to  $C_{10}$  aryl group and a 3 to 10 membered heterocyclic group; or  $R_4$  and  $R_5$  together with the nitrogen atom to which they are attached combine to form a 3 to 10 membered heterocyclic group, wherein said alkyl, alkenyl, cycloalkyl, aryl and heterocyclic groups are unsubstituted or may be  
 25 substituted by one to three groups selected from:  $C_1$  to  $C_6$  alkoxy,  $C_2$  to  $C_8$  alkoxyalkoxy,  $C_3$  to  $C_8$  cycloalkyl,  $C_6$  to  $C_{10}$  aryl, 3 to 10 membered heterocyclic,  $C_7$  to  $C_{10}$  aralkyl, 3 to 10 membered heterocyclic- $C_1$  to  $C_4$  alkyl, -OH, or  $-\text{NR}_j\text{R}_k$ ;  
 $R_j$  and  $R_k$  are independently selected from  $C_1$  to  $C_6$  straight chain or branched alkyl group;

30 n is an integer from about 5 to about 500;

p is an integer from 1 to 12;

t is an integer from 1 to 12; and

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q is greater than zero but less than 1.

The amine-containing polymer described above is an amphiphilic diblock copolymer which has been found to spontaneously form self-assembled reverse micelles in oil-based systems. The incompatibility of the amine-containing polymers with the oil phase has been found by the inventors to be a sufficient driver in itself for self-assembly of the reverse micelle. Meanwhile, formation of the micelles has surprisingly been found to modify the basicity of the amine groups contained in the diblock copolymers, such that their ability to neutralise acid is increased. Thus, as a result of reverse micelle formation in the oil, the  $pK_a$  value of the diblock copolymer has been found by the inventors to increase and the micelles are able to make significant TBN contributions to the oil composition in which they are dispersed. Furthermore, the amine-containing diblock copolymers exhibit good oil solubility and micelle formation also ensures stability in the oil.

The term "ashless TBN booster" used herein is intended to refer to a substance that may contribute towards the Total Base Number (TBN) of an oil of lubricating viscosity in which it is dispersed, without contributing to the level of sulfated ash of the oil composition. Thus, the ashless TBN booster has an affinity for acid and contributes to the oil's overall ability to neutralise acid to which it is exposed, alongside any other basic components of the oil including overbased detergents such as calcium carbonate.

The term "amine-containing diblock copolymer" used herein refers to the copolymers according to Formulae I, II and III, where the term "diblock" is intended to refer to the presence of a hydrophilic amine-containing block or amine-containing copolymer block of n repeat units and a hydrophobic block corresponding to group Z of Formulae I, II and III, which includes hydrocarbyl group,  $R^6$ .

The term "alkyl" as used herein, either alone or as part of another group (e.g. aralalkyl) refers to a monovalent saturated aliphatic group, including straight-chain and branched groups. Examples of alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, neopentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl and n-octadecyl.

The term "cycloalkyl" as used herein refers to a monovalent saturated aliphatic group containing at least one ring, wherein said ring has at least 3 ring carbon atoms. Examples of cycloalkyl groups include groups that are monocyclic, polycyclic (e.g. bicyclic) or

bridged ring system. Examples of cycloalkyl groups include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and the like. The term "cycloalkylene" as used herein refers to a corresponding divalent moiety.

The term "alkenyl" as used herein refers to a monovalent straight-chain or branched alkyl group containing at least one carbon-carbon double bond, of either E or Z configuration unless specified. Examples of alkenyl groups include ethenyl, 2-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl and the like.

The term "alkynyl" as used herein refers to a monovalent alkyl group containing at least one carbon-carbon triple bond.

The term "aryl" as used herein refers to an aromatic carbocyclic ring system. An example of an aryl group includes a group that is a monocyclic aromatic ring system or a polycyclic ring system containing two or more rings, at least one of which is aromatic. Examples of aryl groups include aryl groups that comprise from 1 to 6 exocyclic carbon atoms in addition to ring carbon atoms. Examples of aryl groups include aryl groups that are monovalent or polyvalent as appropriate. Examples of monovalent aryl groups include phenyl, benzyl naphthyl, fluorenyl, azulenyl, indenyl, anthryl and the like. An example of a divalent aryl group is 1,4-phenylene.

The term "alkylene" refers to a divalent straight or branched chain saturated hydrocarbyl group containing from 1 to 30 carbon atoms. Examples of alkylene groups include alkylene groups that contain from 1 to 20 carbon atoms, e.g. from 1 to 12 carbon atoms, e.g. from 1 to 10 carbon atoms. Particular examples include alkylene groups that contain 1, 2, 3, 4, 5 or 6 carbon atoms.

The term "alkoxy" as used herein refers to -O-alkyl, wherein alkyl is as defined herein. Examples of alkoxy groups include methoxy, ethoxy, propoxy, isopropoxy, butoxy, tert-butoxy, pentoxy, hexoxy and the like.

The term "heterocyclic" as used herein refers to a saturated, unsaturated or aromatic cyclic or fused polycyclic moiety, wherein the ring atoms include at least one ring carbon atom and at least one ring heteroatom selected from nitrogen, oxygen and sulphur. Examples of heterocyclic groups include heterocyclic groups that contain from 3 to 10 ring atoms, e.g. from 3 to 6 ring atoms. Particular examples include heterocyclic groups that contain 5 or 6 ring atoms, including for example, groups that are saturated, unsaturated or

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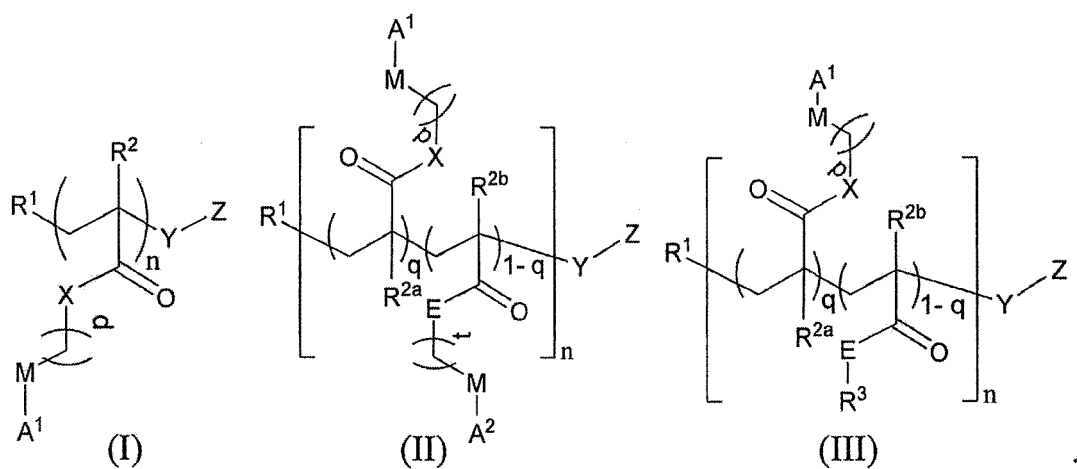
aromatic. Examples of heterocyclic groups include ethylene oxide, azetidiny, pyrrolidinyl, pyrrolyl, pyrazolyl, oxetanyl, pyrazolinyl, imidazolyl, imidazolinyl, imidazolidinyl, oxazolyl, oxazolidinyl, isoxazolinyl, isoxazolyl, thiazolyl, thiadiazolyl, thiazolidinyl, isothiazolyl, isothiazolidinyl, furyl, tetrahydrofuryl, thienyl, oxadiazolyl, piperidinyl, piperazinyl, azepinyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, triazinyl, triazolyl, tetrazolyl, tetrahydropyranyl, morpholinyl, thiamorpholinyl. Examples of heterocyclic groups include those that are monovalent or polyvalent as appropriate.

The term "aliphatic hydrocarbyl" as used herein refers to a saturated or unsaturated, optionally substituted group comprising at least 90 % by molecular weight of hydrogen and carbon atoms. Examples of hydrocarbyl groups include acyclic groups, cyclic groups and groups comprising both an acyclic portion and a cyclic portion. Examples of hydrocarbyl groups include linear groups and branched groups. The term "hydrocarbyl" includes monovalent groups and polyvalent groups as specified. Examples of monovalent hydrocarbyl groups include alkyl, alkenyl, alkynyl, and cycloalkyl.

The term "optionally substituted" as used herein means unsubstituted or substituted.

The term "substituted" as used herein as used in connection with a chemical group means that one or more (e.g. 1, 2, 3, 4 or 5) of the hydrogen atoms in that group are replaced independently of each other by a corresponding number of substituents. When present, the one or more substituents are present only at positions where they are chemically possible, i.e. that any substitution is in accordance with permitted valence of the substituted atom and the substituent and that the substitution results in a stable compound. Examples of substituents include -CN, -OH, -SH, -NO<sub>2</sub>, -CO<sub>2</sub>R<sup>x</sup>, -OC(O)R<sup>x</sup>, -C(O)R<sup>x</sup>, C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>6</sub> to C<sub>10</sub> aryl, 3 to 10 membered heterocyclic, C<sub>7</sub> to C<sub>10</sub> aralkyl, and 3 to 10 membered heterocyclic-C<sub>1</sub> to C<sub>4</sub> alkyl, wherein R<sup>x</sup> is selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl.

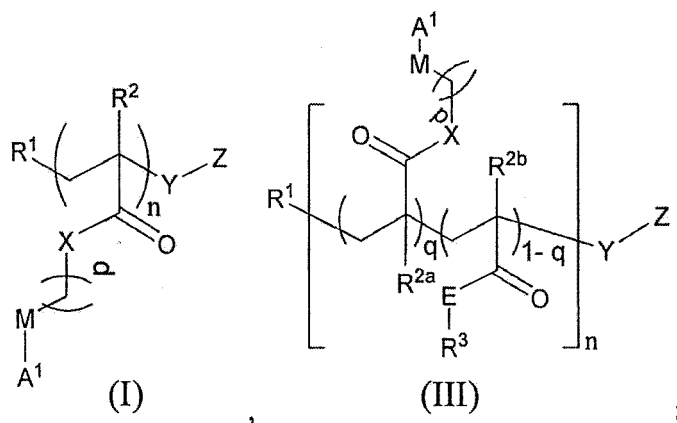
The lubricating composition according to embodiments of the present invention comprises an ashless TBN booster selected from an amine-containing amphiphilic diblock copolymer according to Formula I, II and/or III:



wherein  $R^1$  to  $R^3$ ,  $A^1$ ,  $A^2$ ,  $M$ ,  $E$ ,  $X$ ,  $Y$ ,  $Z$ ,  $n$ ,  $t$ ,  $p$  and  $q$  are as defined hereinabove. The composition may comprise a single diblock copolymer according to any of Formula I, II or III. Alternatively, mixtures of different diblock copolymers according to Formula I, II or

5 III may be used in the same lubricating composition.

In some embodiments, the lubricating composition according to the present invention comprises an ashless TBN booster selected from an amine-containing amphiphilic diblock copolymer according to Formula I and/or III:

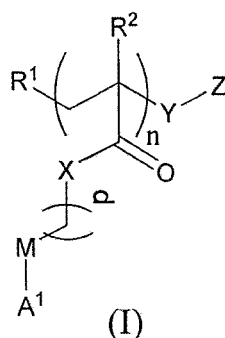


10 wherein  $R^1$  to  $R^3$ ,  $A^1$ ,  $A^2$ ,  $M$ ,  $E$ ,  $X$ ,  $Y$ ,  $Z$ ,  $n$ ,  $t$ ,  $p$  and  $q$  are as defined hereinabove.

In some embodiments, the lubricating composition comprises an ashless TBN booster selected from an amine-containing amphiphilic diblock copolymer according to Formula I:

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wherein:

$R^1$  is a  $C_1$  to  $C_{12}$  straight chain or branched alkyl group, a  $C_6$  to  $C_{10}$  aryl group or a 3 to 10 membered heterocyclic group, wherein said alkyl, aryl or heterocyclic groups may be unsubstituted or substituted;

$R^2$  is H or methyl;

$R^3$  is a  $C_1$ - $C_{24}$  straight chain or branched alkyl group;

X is O or NH;

Y is S, S(=O), or S(=O)<sub>2</sub>;

Z is selected from:

-CH<sub>2</sub>CH<sub>2</sub>-C(=O)-O-R<sup>6</sup>, -CH<sub>2</sub>CH<sub>2</sub>-C(=O)-R<sup>6</sup>, -CH<sub>2</sub>CH<sub>2</sub>-C(=O)-S-R<sup>6</sup>,  
-CH<sub>2</sub>CH<sub>2</sub>-C(=O)-NH-R<sup>6</sup>, -CH<sub>2</sub>CH<sub>2</sub>-C(=S)-NH-R<sup>6</sup>, and  
-CH(-CH<sub>2</sub>-C(=O)-O-R<sup>6</sup>)(-C(=O)-O-R<sup>6</sup>);

R<sup>6</sup> is a  $C_6$  to  $C_{50}$  aliphatic hydrocarbyl group;

M is CH<sub>2</sub>;

A<sup>1</sup> is selected from NR<sup>4</sup>R<sup>5</sup>, a 3 to 10 membered heterocyclic group containing a nitrogen ring atom which is not attached to M via a nitrogen atom, or a  $C_6$  to  $C_{10}$  aryl group substituted by 1 to 2 -NR<sub>j</sub>R<sub>k</sub> groups;

R<sup>4</sup> and R<sup>5</sup> are independently selected from hydrogen, a  $C_1$  to  $C_8$  straight chain or branched alkyl group, a  $C_2$  to  $C_8$  straight chain or branched alkenyl group, a  $C_3$  to  $C_8$  cycloalkyl group, a  $C_6$  to  $C_{10}$  aryl group and a 3 to 10 membered heterocyclic group; or R<sup>4</sup> and R<sup>5</sup> together with the nitrogen atom to which they are attached combine to form a 3 to 10 membered heterocyclic group, wherein said alkyl, alkenyl, cycloalkyl, aryl and heterocyclic groups are unsubstituted or may be substituted by one to three groups selected from:  $C_1$  to  $C_6$  alkoxy,  $C_2$  to  $C_8$

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alkoxyalkoxy, C<sub>3</sub> to C<sub>8</sub> cycloalkyl, C<sub>6</sub> to C<sub>10</sub> aryl, 3 to 10 membered heterocyclic, C<sub>7</sub> to C<sub>10</sub> aralkyl, 3 to 10 membered heterocyclic-C<sub>1</sub> to C<sub>4</sub> alkyl, -OH, or -NR<sub>j</sub>R<sub>k</sub>; R<sub>j</sub> and R<sub>k</sub> are independently selected from C<sub>1</sub> to C<sub>6</sub> straight chain or branched alkyl group;

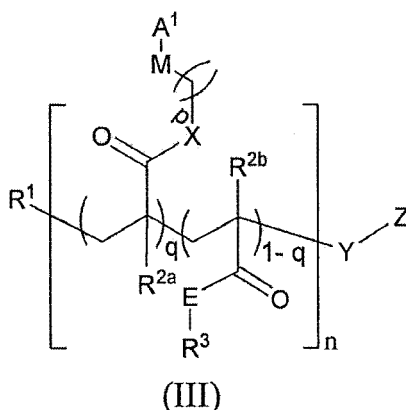
5 n is an integer from about 5 to about 500;

p is an integer from 1 to 12; and

q is greater than zero but less than 1.

In other embodiments, the ashless TBN booster is selected from an amine-containing amphiphilic diblock copolymer according to Formula III:

10



wherein:

R<sup>1</sup> is a C<sub>1</sub> to C<sub>12</sub> straight chain or branched alkyl group, a C<sub>6</sub> to C<sub>10</sub> aryl group or a 3 to 10 membered heterocyclic group, wherein said alkyl, aryl or heterocyclic groups

15 may be unsubstituted or substituted;

R<sup>2</sup>, R<sup>2a</sup> and R<sup>2b</sup> are independently H or methyl;

R<sup>3</sup> is a C<sub>1</sub>-C<sub>24</sub> straight chain or branched alkyl group;

E is O or NH;

X is O or NH;

20 Y is S, S(=O), or S(=O)<sub>2</sub>;

Z is selected from:

-CH<sub>2</sub>CH<sub>2</sub>-C(=O)-O-R<sup>6</sup>, -CH<sub>2</sub>CH<sub>2</sub>-C(=O)-R<sup>6</sup>, -CH<sub>2</sub>CH<sub>2</sub>-C(=O)-S-R<sup>6</sup>,

-CH<sub>2</sub>CH<sub>2</sub>-C(=O)-NH-R<sup>6</sup>, -CH<sub>2</sub>CH<sub>2</sub>-C(=S)-NH-R<sup>6</sup>, and

-CH(-CH<sub>2</sub>-C(=O)-O-R<sup>6</sup>)(-C(=O)-O-R<sup>6</sup>);

25 R<sup>6</sup> is a C<sub>6</sub> to C<sub>50</sub> aliphatic hydrocarbyl group;

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M is CH<sub>2</sub>;

A<sup>1</sup> is selected from NR<sup>4</sup>R<sup>5</sup>, a 3 to 10 membered heterocyclic group containing a nitrogen ring atom which is not attached to M via a nitrogen atom, or a C<sub>6</sub> to C<sub>10</sub> aryl group substituted by 1 to 2 -NR<sub>j</sub>R<sub>k</sub> groups;

5 R<sup>4</sup> and R<sup>5</sup> are independently selected from hydrogen, a C<sub>1</sub> to C<sub>8</sub> straight chain or branched alkyl group, a C<sub>2</sub> to C<sub>8</sub> straight chain or branched alkenyl group, a C<sub>3</sub> to C<sub>8</sub> cycloalkyl group, a C<sub>6</sub> to C<sub>10</sub> aryl group and a 3 to 10 membered heterocyclic group; or R<sub>4</sub> and R<sub>5</sub> together with the nitrogen atom to which they are attached combine to form a 3 to 10 membered heterocyclic group, wherein said alkyl,  
10 alkenyl, cycloalkyl, aryl and heterocyclic groups are unsubstituted or may be substituted by one to three groups selected from: C<sub>1</sub> to C<sub>6</sub> alkoxy, C<sub>2</sub> to C<sub>8</sub> alkoxyalkoxy, C<sub>3</sub> to C<sub>8</sub> cycloalkyl, C<sub>6</sub> to C<sub>10</sub> aryl, 3 to 10 membered heterocyclic, C<sub>7</sub> to C<sub>10</sub> aralkyl, 3 to 10 membered heterocyclic-C<sub>1</sub> to C<sub>4</sub> alkyl, -OH, or -NR<sub>j</sub>R<sub>k</sub>;  
R<sub>j</sub> and R<sub>k</sub> are independently selected from C<sub>1</sub> to C<sub>6</sub> straight chain or branched alkyl  
15 group;

n is an integer from about 5 to about 500;

p is an integer from 1 to 12; and

q is greater than zero but less than 1.

In some embodiments, R<sup>1</sup> of Formula I, II or III is unsubstituted or substituted by one  
20 to three groups selected from: -CN, -OH, -SH, -NO<sub>2</sub>, -CO<sub>2</sub>R<sup>x</sup>, -OC(O)R<sup>x</sup>, -C(O)R<sup>x</sup>, C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>6</sub> to C<sub>10</sub> aryl, 3 to 10 membered heterocyclic, C<sub>7</sub> to C<sub>10</sub> aralkyl, and 3 to 10 membered heterocyclic-C<sub>1</sub> to C<sub>4</sub> alkyl, wherein R<sup>x</sup> is selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl.

In some embodiments, R<sup>1</sup> of Formula I, II or III is unsubstituted or substituted by one  
25 to three groups selected from: -CN, -OH, -SH, -NO<sub>2</sub>, -CO<sub>2</sub>R<sup>x</sup>, and -OC(O)R<sup>x</sup>, wherein R<sup>x</sup> is selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl. In other embodiments, R<sup>1</sup> is unsubstituted or substituted by one to three groups selected from: -CN, -CO<sub>2</sub>R<sup>x</sup>, and -OC(O)R<sup>x</sup>, wherein R<sup>x</sup> is selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl, for example wherein R<sup>1</sup> is unsubstituted or substituted by a single -CN group.

30 In some embodiments, R<sup>1</sup> of Formula I, II or III is a C<sub>1</sub> to C<sub>6</sub> straight chain or branched alkyl group.

In some embodiments, R<sup>1</sup> of Formula I, II or III is a C<sub>3</sub> to C<sub>6</sub> branched alkyl group.

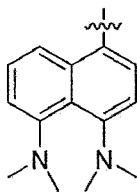
In some embodiments,  $R^1$  of Formula I, II or III is  $-\text{CH}(\text{CH}_2)_2\text{CN}$ .

In some embodiments,  $R^2$ ,  $R^{2a}$  and/or  $R^{2b}$  of Formula I, II or III as applicable is/are methyl.

In some embodiments,  $A^1$  and/or  $A^2$  of Formula I, II or III as applicable is/are  $\text{NR}^4\text{R}^5$ . In embodiments,  $R^4$  and  $R^5$  are independently selected from a  $\text{C}_1$  to  $\text{C}_4$  straight chain or branched alkyl group. In exemplary embodiments,  $R^4$  and  $R^5$  are both a methyl or both an ethyl group. In other embodiments,  $R^4$  and  $R^5$  together with the nitrogen atom to which they are attached combine to form a 3 to 10 membered heterocyclic group. In exemplary embodiments, the heterocyclic group is a morpholinyl or pyridyl group.

In some embodiments,  $A^1$  and/or  $A^2$  of Formula I, II or III as applicable is/are a 3 to 10 membered heterocyclic group containing a nitrogen ring atom which is not attached to M via a nitrogen atom, for example wherein the heterocyclic group is pyridyl.

In some embodiments,  $A^1$  and/or  $A^2$  of Formula I, II or III as applicable is/are a  $\text{C}_6$  to  $\text{C}_{10}$  aryl group substituted by 1 to 2  $-\text{NR}_j\text{R}_k$  groups, for example an aryl group having the structure:



In some embodiments,  $R^3$  of Formula III is a  $\text{C}_1$ - $\text{C}_{18}$  straight chain or branched alkyl group.

In some embodiments,  $R^3$  of Formula III is a  $\text{C}_6$ - $\text{C}_{14}$  straight chain alkyl group, for example a  $\text{C}_{12}$  straight chain alkyl group.

In some embodiments, E and/or X of Formula I, II or III as applicable is/are O.

In some embodiments, Y of Formula I, II or III is S.

In some embodiments, Z of Formula I, II or III is selected from:  $-\text{CH}_2\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{R}^6$  and  $-\text{CH}(-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{R}^6)(-\text{C}(=\text{O})-\text{O}-\text{R}^6)$ .

In some embodiments,  $R^6$  of Formula I, II or III is a  $\text{C}_{16}$  to  $\text{C}_{30}$  aliphatic hydrocarbyl group, for example  $-(\text{CH}_2)_8\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3$  or  $-(\text{CH}_2)_{21}\text{CH}_3$ .

In some embodiments, n of Formula I, II or III is an integer from about 5 to about 100. In some embodiments, n of Formula I, II or III is an integer from about 5 to about 50. In some embodiments, n of Formula I, II or III is an integer from about 5 to about 25.

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In some embodiments, p of Formula I, II or III is an integer from 1 to 3, for example 1.

In some embodiments, t of Formula I, II or III is an integer from 1 to 3, for example 1.

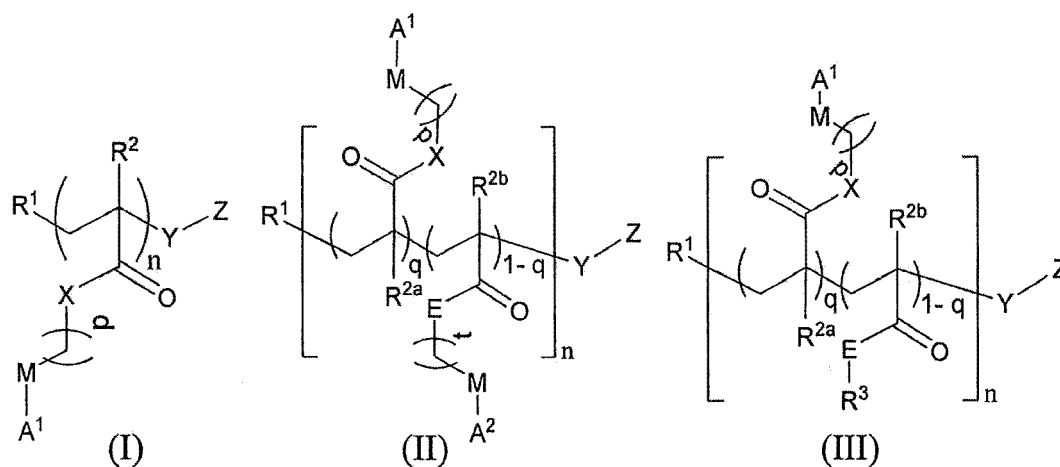
5 In some embodiments, q of Formula I, II or III is from 0.20 to 0.80, for example from 0.50 to 0.80.

In some embodiments, the molecular weight of the diblock-copolymer is from about 0.5 to about 120 kDa. In other embodiments, the molecular weight of the diblock-copolymer is from about 20 to about 90 kDa.

10 In some examples, the amine-containing diblock copolymer of Formula I, II or III has a nitrogen content of from about 1 to about 10 mol.%. In other examples, the amine-containing diblock copolymer of Formula I or II has a nitrogen content of from about 6 to about 9 mol.%. In other examples, the amine-containing diblock copolymer of Formula III has a nitrogen content of from about 2 to about 7 mol.%.

15 The amine-containing diblock copolymers according to Formula I, II and III described hereinbefore have good oil solubility and spontaneously form reverse micelles in oil. Advantageously, the reverse micelles themselves have been found by the inventors to have a high degree of stability in oil compositions, making them particularly suitable for formulating with lubricating oil compositions. Spontaneous micelle formation in oil has  
20 also surprisingly been found by the inventors to enhance the basic properties of the amine-containing hydrophilic block of the amphiphilic diblock copolymer, so as to increase the acid neutralising properties. This is, for example, illustrated by an increase in the  $pK_a$  of the polymer upon modification by tethering a hydrophobic block to afford the necessary amphiphilic properties required for micelle formation. The amine-containing diblock  
25 copolymers according to Formulae I, II and III described herein represent ashless sources of base that may be used effectively as ashless TBN boosters, including in lubricating oil formulations having a variety of common viscosity grades (e.g. 0W, 5W, 10W, 20W-20, 30, 40 and 50).

Thus, the present invention also provides an amine-containing diblock copolymer of  
30 Formula I, II or III:



wherein  $R^1$  to  $R^3$ ,  $A^1$ ,  $A^2$ ,  $M$ ,  $E$ ,  $X$ ,  $Y$ ,  $Z$ ,  $n$ ,  $t$ ,  $p$  and  $q$  are as defined hereinbefore.

The hydrophilic portion of the amphiphilic diblock copolymer which comprises the  $n$  repeat units of a tertiary amine containing moiety provides the basic components of the TBN booster. Meanwhile, the hydrophobic portion of the amphiphilic diblock copolymer, forming the group  $Z$  recited in Formula I, II and III, comprises an aliphatic hydrocarbyl group,  $R^6$ , which confers oil solubility on the polymer. Moreover, the amphiphilic properties conferred by the presence of distinct hydrophilic and hydrophobic portions means that the diblock copolymer readily forms a reverse micelle in an oil-based composition. The reverse micelle assembly positions the hydrophilic amine-containing portion of the amphiphilic diblock copolymer towards the centre of the micelle, forming a dense core, whilst the hydrophobic portions of the diblock copolymer extend outwards toward the oil-based solvent, thereby forming a corona.

Reverse micelle formation and the production of a dense polar core has been found by the inventors to increase the basicity of the amine groups, thereby enhancing the acid scavenging ability, which may, for instance, be verified through changes in  $pK_a$  values. Without being bound by any particular theory, this is believed to be a result of increased cooperative basicity between amine groups which occupy the dense polar core of the micelle.

The effect of the invention is considered to be well illustrated by increases in  $pK_a$  values upon reverse micelle formation in oil. Measured TBN values may also demonstrate the effects of the invention. TBN values provide information as to the number of reactive basic constituents assessed on the basis of titration.

The most common ASTM methods for determining TBN in lubricating oil compositions are presently D4739 and D2896. ASTM D4739 is principally relied upon for used oil analysis whilst ASTM D2896 is often used in fresh oil specifications. Both methods rely on acid titration as a means for deriving a neutralisation number, expressed as the TBN. ASTM D4739 involves a potentiometric hydrochloric acid titration with a non-polar toluene/IPA/chloroform solvent system. ASTM D2896 instead involves a potentiometric titration with perchloric acid in glacial acetic acid using a chlorobenzene/glacial acetic acid mixed solvent.

The combination of a stronger acid and a more polar solvent employed in ASTM D2896, as compared with ASTM D4739, means that all salts that are present, even those formed during the titration itself, are titrated in the method of ASTM D2896 as if they were basic. Moreover, the presence of acetic acid in the solvent system of ASTM D2896 has the capacity to interfere with the equilibrium that exists between amine groups and the corresponding ammonium salt. By contrast, the non-polar solvent and weaker acid used in ASTM D4739 means that salts are not titrated in that method and, in the context of the present invention, only amine groups are titrated. Thus, whilst the titration method according to ASTM D4739 may provide more of an accurate representation of the TBN value of the lubricating compositions according to embodiments of the invention compared to ASTM D2896, there remains the issue that ASTM D4739 is designed specifically for used oils and not fresh lubricant compositions.

Consequently, in the context of the present invention, neither ASTM D2896 nor ASTM D4739 alone can be considered to be entirely suitable for determining the true TBN of a lubricating composition according to embodiments of the invention. Nevertheless, using one of these methods, more preferably ASTM D2896, in conjunction with  $pK_a$  determination gives a true representation of the contribution made by a diblock copolymer according to Formula I, II or III to the TBN value and affinity to interact with acids in a lubricant. Thus,  $pK_a$  values obtained for the diblock copolymer are considered to be a particularly reliable representation of the effects of the invention. A suitable method for determining the  $pK_a$  of the diblock copolymers used in accordance with embodiments of the present invention is described hereinbelow.  $pK_a$  values are a quantitative measure of the strength of an acid or base in a solvent. Increases in  $pK_a$  values associated with micelle formation demonstrate that this change in architecture increases the strength of the basic

groups that are present. Without being bound by any particular theory, it is believed that micelle formation is beneficial for positioning basic groups so as to enhance their effective basicity by means of a cooperative basicity effect.

In embodiments, basicity of the amine groups of the amine-containing amphiphilic diblock copolymer according to the invention is further enhanced by incorporating interposing non-polar hydrophobic moieties between amine groups on the polymer chain. Proximal amine groups can negatively impact upon each other's basicity. For example, once an amine group becomes a charged ammonium cation through basic reaction, proximal amine groups may to some extent be prevented from undergoing basic reaction, which would otherwise form a further cationic group, as a result of unfavourable charge proximity. Amine groups on adjacent polymer chains can also experience steric hindrance which can impact upon their basicity. By interposing non-polar hydrophobic groups between amine moieties on the polymer chain by co-polymerisation, it is believed that charge proximity and steric hindrance between adjacent polymer chains becomes less of an issue and the basicity of individual amine groups is not impacted to such a degree.

Therefore, paradoxically, reducing the concentration of amine groups on the hydrophilic portion of the diblock copolymer has been found by the inventors to further enhance the basicity of the amine-containing diblock copolymer. As a result of the reduced hydrophilicity of the amine-containing portion of the diblock copolymer, oil solubility is also advantageously increased, without impacting upon micelle formation, as verified by dynamic light scattering (DLS) characterisations. Embodiments where the amphiphilic diblock copolymers are in accordance with Formula III described hereinbefore, which have a hydrophilic amine-containing portion formed from the copolymerisation of an amine-containing monomer and a hydrophobic monomer, will therefore benefit from further enhanced basicity, oil solubility and elastomer compatibility.

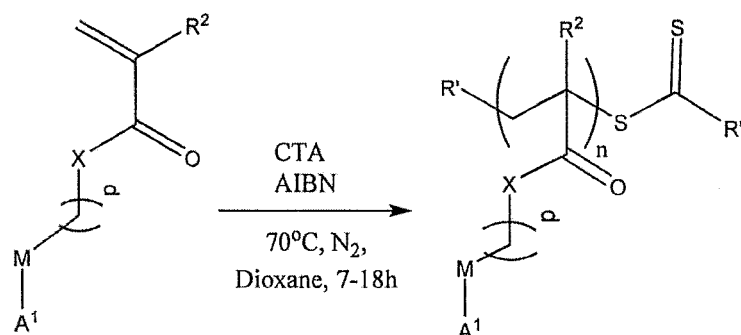
Amphiphilic diblock copolymers according to Formulae I, II and III may be well tolerated by seal materials. Indeed, it may be unnecessary to modify the polarity and the abundance of the amine groups in a molecule so as to reduce swelling and deformation effects normally associated therewith.

The amphiphilic diblock copolymers according to Formula I, II and III may suitably be prepared using reversible addition-fragmentation chain transfer (RAFT) followed by end-group modification, for instance by Michael addition. In comparison to free radical

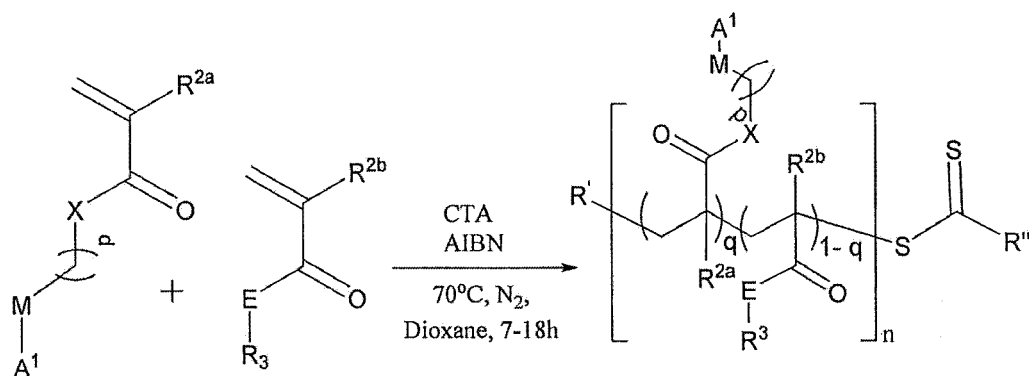
polymerisation, which gives broad polymer molecular weight distributions and uncertainty as to polymer structure, RAFT allows a high level of control such that certain polymer properties, such as molecular weight and polydispersity, can be tuned. The diblock copolymers according to Formula II and III described herein comprise an amine containing a randomly distributed statistical copolymer portion, where monomers are randomly distributed along the polymer chain.

Suitable methods for forming the amine-containing homo- or co-polymer by RAFT polymerisation, followed thereafter by end group modification to produce a diblock copolymer, are described, for instance, in *Chem. Soc. Rev.*, 2014, 43, 496-505; *J Polym Sci Part A: Polym Chem.*, 2005, 43, 5347-5393; and *Polym Int.*, 2000, 49, 993-1001. One such method for preparation of a homopolymer of an amine monomer by RAFT polymerisation involves admixing the amine monomer with a RAFT chain transfer agent, azo initiator (e.g. AIBN) and a solvent (e.g. dioxane) in an inert atmosphere, before heating, for example at 70°C for 7 hours. Preparation of an amine-containing copolymer differs only in that two different monomers are admixed. These reactions are illustrated in the Schemes I and II below.

Scheme I:



Scheme II:

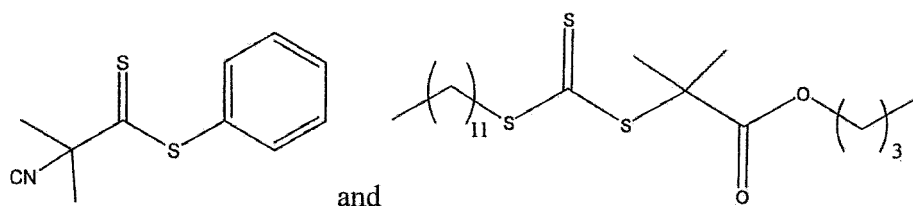


As illustrated above, both end groups of the RAFT derived polymer ( $-\text{SC}(=\text{S})\text{R}''$  and  $-\text{R}'$ ) derive from the particular chain transfer agent (CTA) used for the polymerisation. As part of the preparation of diblock copolymers according to Formula I, II and III, the dithioester end group is modified, as described in more detail below. The other end group

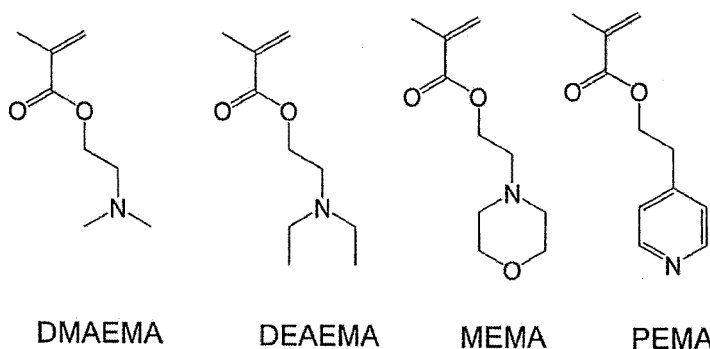
5 ( $-\text{R}'$ ) may suitably be unmodified or modified as desired. Selection of the CTA may thus allow a selection of the particular non-dithioester end group which is incorporated into the diblock copolymer according to Formula I, II and III (corresponding to group  $\text{R}^1$  therein)

Preferred chain transfer agents for preparation of diblock copolymers according to Formula I, II and III are 2-cyanoprop-2-yl-dithiobenzoate (CDB) and

10 3-Butyl 2-(dodecylthiocarbonothioylthio)-2-methylpropionate illustrated below, both of which are commercially available and readily scalable:



15 Preferred amine monomers for RAFT homo- or co-polymerisation include those selected from the following:

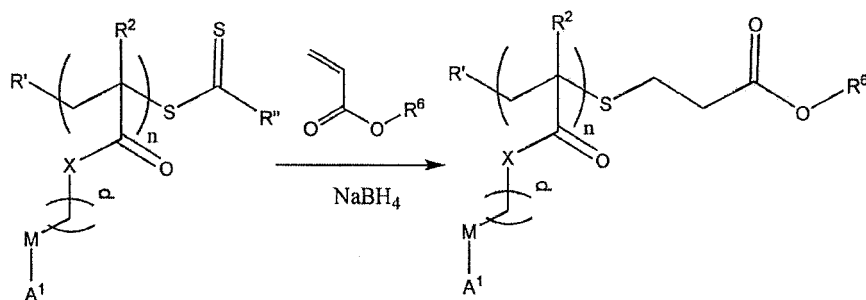


In order to obtain an amphiphilic diblock copolymer according to Formula I, II or III, from the RAFT derived polymer, the dithioester end group is modified, for instance, by

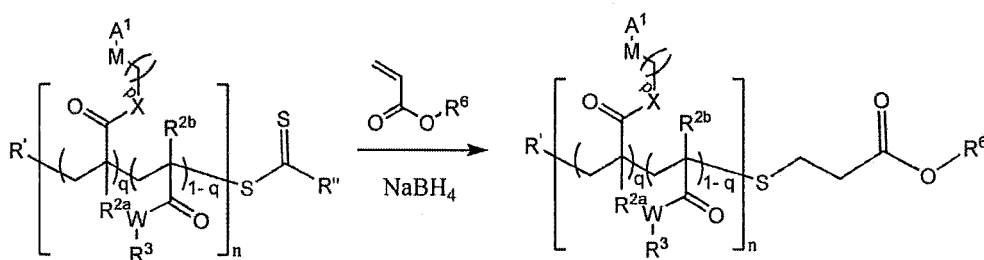
20 reaction with a Michael acceptor which allows addition of an aliphatic polymeric unit, thereby forming a diblock copolymer. For example, the amine-containing dithioester terminated polymer may be admixed with an alkyl acrylate group in a suitable solvent (e.g. THF) and reacted under inert atmosphere in the presence of sodium borohydride and

tributyl phosphine to form the corresponding diblock copolymer, as illustrated in Schemes III and IV below.

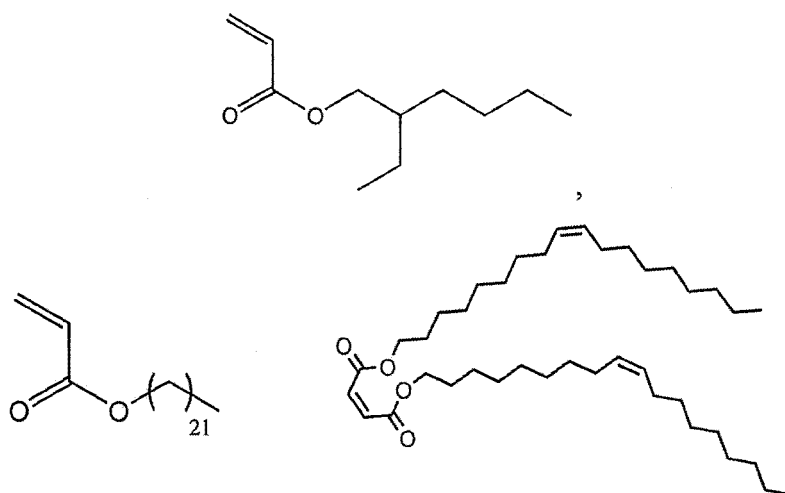
Scheme III:

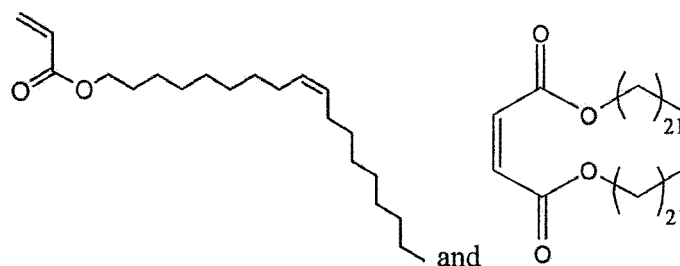


Scheme IV:



10 Preferred Michael acceptors for end group modification include:





The diblock copolymer obtained may be purified by any suitable means of which the skilled person is aware, such as by precipitation and/or chromatography. Suitable precipitation solvents include diethyl ether or methanol. The diblock copolymers formed may readily be characterised by size exclusion chromatography (SEC) and  $^1\text{H}$  NMR.

In the preparation of a lubricating composition according to an aspect of the present invention, a base oil of lubricating viscosity may be admixed with an amount of the diblock copolymer according to Formula I, II and/or III together with one or more lubricant additives. The critical micelle concentration (i.e. the concentration of the amphiphilic diblock copolymer in an oil-based system at which micelles form) has been found to be particularly low with the amphiphilic diblock copolymers according to Formula I, II and III and well below the typical concentration of diblock copolymers used for TBN boosting in a lubricating composition.

The concentration of diblock copolymer according to Formula I, II and/or III in the lubricating compositions according to the invention is suitably about 0.2 % by weight or above, about 0.5 % by weight or above, about 1.0 % by weight or above, about 1.5 % by weight or above, or about 2% by weight above. The upper limit of diblock copolymer according to Formula I, II and/or III in the lubricating composition according to an aspect of the invention is suitably about 3.0% by weight, about 4 % by weight, about 5 % by weight, about 6 % by weight, or about 7 % by weight. In exemplary embodiments, the concentration of diblock copolymer according to Formula I, II and/or III in the lubricating compositions according to the invention is from about 0.2 % by weight to about 7 % by weight. In other exemplary embodiments, the concentration of diblock copolymer according to Formula I, II and/or III in the lubricating compositions according to the invention is from about 3.0% by weight to about 6 % by weight.

In some examples, the lubricating composition comprises an amount of diblock copolymer according to Formula I, II and/or III which contributes about 0.5 to about 10 mg

KOH/g, about 1 to about 8 mg KOH/g, or about 3 to about 6 mg KOH/g to the TBN of the lubricating composition, as measured in accordance with ASTM D2896.

In some examples, the lubricating composition according to embodiments of the present invention derives at least about 5 %, at least about 10 %, at least about 20 %, or  
5 even at least about 30 % of its TBN value from the presence of diblock copolymer according to Formula I, II and/or III.

In some examples, the amphiphilic diblock copolymer has a TBN of at least about 50 mg KOH/g, at least about 100 mg KOH/g, or even at least about 150 mg KOH/g, as measured in accordance with ASTM D2896. In exemplary embodiments, the amphiphilic  
10 diblock copolymer has a BN of from 50 to 300 mg KOH/g, as measured in accordance with ASTM D2896. In other exemplary embodiments, the amphiphilic diblock copolymer has a BN of from 100 to 250 mg KOH/g, as measured in accordance with ASTM D2896.

In some examples, the lubricating compositions according to embodiments of the present invention have a TBN of at least about 5 mg KOH/g, at least about 10 mg KOH/g  
15 or at least about 15 mg KOH/g, as measured in accordance with ASTM D2896. In exemplary embodiments, the lubricating compositions according to the present invention have a TBN of from about 5 mg KOH/g to about 20 mg KOH/g.

In some example, for instance where the lubricating composition is intended for use in marine applications, the lubricating composition may have a TBN of at least about 30,  
20 as measured in accordance with ASTM D2896. In exemplary embodiments, the lubricating compositions according to embodiments of the present invention have a TBN of from about 30 mg KOH/g to about 50 mg KOH/g.

In some examples, the amphiphilic diblock copolymer has a  $pK_a$  of at least about 7.5 KOH/g, at least about 8, at least about 9, or even at least about 10.0, as measured using a  
25 potentiometric titration with glacial acetic acid using an acetonitrile solvent. In exemplary embodiments, the amphiphilic diblock copolymer has a  $pK_a$  of from about 7.5 to about 12 or from about 9 to about 11, as measured using a potentiometric titration with glacial acetic acid using an acetonitrile solvent.

The lubricating composition of the invention suitably comprises a major amount of  
30 base oil and a minor amount of one or more lubricant additives. Major amount means at least 50% by weight, for example greater than 50% by weight. Minor amount means less than 50% by weight. Suitably, the lubricating composition of the invention comprises at

least about 60% by weight of base oil, at least about 70% by weight of base oil, at least about 80% by weight of base oil, or at least about 90% by weight of base oil.

The nature of the base oil is not particularly limited and the skilled person is able to select a suitable base oil based on the particular intended use of the lubricating

- 5 composition. Lubricant base stocks used in automotive and marine engine lubricants are generally obtained from petrochemical sources, for example as the higher boiling fractions isolated during the refining of crude oil or as the products of chemical reactions of feedstocks from petrochemical sources. Lubricant base stocks can also be made from Fischer-Tropsch wax.

- 10 Lubricant base stocks may be classified as Group I, II, III, IV and V base stocks according to API standard 1509, "ENGINE OIL LICENSING AND CERTIFICATION SYSTEM", September 2012 version 17<sup>th</sup> edition Appendix E, as set out in the table below:

| Group | Saturated hydrocarbon content (% by weight) ASTM D2007 |        | Sulphur content (% by weight) ASTM D2622 or D4294 or D4927 or D3120 |     | Viscosity Index ASTM D2270 |
|-------|--------------------------------------------------------|--------|---------------------------------------------------------------------|-----|----------------------------|
| I     | < 90                                                   | and/or | > 0.03                                                              | and | ≥ 80 and < 120             |
| II    | ≥ 90                                                   | and    | ≤ 0.03                                                              | and | ≥ 80 and < 120             |
| III   | ≥ 90                                                   | and    | ≤ 0.03                                                              | and | ≥ 120                      |
| IV    | polyalphaolefins                                       |        |                                                                     |     |                            |
| V     | all base stocks not in Groups I, II, III or IV         |        |                                                                     |     |                            |

Group I, Group II and Group III base stocks are generally derived from mineral oils.

- 15 Group I base stocks are typically manufactured by known processes comprising solvent extraction and solvent dewaxing, or solvent extraction and catalytic dewaxing. Group II and Group III base stocks are typically manufactured by known processes comprising catalytic hydrogenation and/or catalytic hydrocracking, and catalytic hydroisomerisation. Group II basestocks include Group II+ basestocks which are Group II basestocks with a viscosity index of 110 to 120. Group IV base stocks include for example, hydrogenated
- 20 oligomers of alpha olefins. Suitable processes for the preparation of the oligomers include for example, free radical processes, Zeigler catalysed processes and cationic Friedel-Crafts

catalysed processes. Suitably, polyalphaolefin base stocks are derived for example from C<sub>8</sub>, C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub> olefins and mixtures of one or more thereof. Thus, the base oil for a lubricating composition according to embodiments of the present invention may comprise or consist of at least one base stock selected from Group I, Group II, Group III, Group IV  
5 and Group V base stocks and mixtures thereof.

In some examples, the base oil of the lubricating composition according to embodiments of the present invention comprises one or more base stocks selected from the group consisting of base stocks derived from Fischer-Tropsch synthesised, waxy, paraffinic hydrocarbon material by processes comprising hydrocracking and/or  
10 hydroisomerisation, Group II basestocks, Group III basestocks and mixtures thereof.

Base stocks derived from Fischer-Tropsch synthesised, waxy, paraffinic hydrocarbon material may be made by processes comprising hydrocracking and/or hydroisomerisation known in the art, for example as described in WO 00/14187, WO 02/064710, WO 2005/066314 and US 6008164.

15 The lubricating composition according to embodiments of the present invention may be a monograde lubricating oil composition according to API classification, for example SAE 20, 30, 40, 50 or 60 grade. Alternatively, the lubricating composition according to embodiments of the present invention may be a multi-grade lubricating composition according to the API classification xW-y where x is 0, 5, 10, 15 or 20 and y is 20, 30, 40,  
20 50 or 60 as defined by SAE J300 2004, for example 5W-20, 5W-30, 0W-20. The lubricating composition may have an HTHS viscosity at 150 °C of at least 2.6cP, for example as measured according to ASTM D4683, CEC L-36-A-90 or ASTM D5481.

The lubricating composition may have an HTHS viscosity at 150 °C according to ASTM D4683 of from 1 to < 2.6cP, for example 1.8cP.

25 In some examples, the base oil has a kinematic viscosity at 100 °C in the range of from 2.5 to 37 mm<sup>2</sup>/s, in the range of from 2.5 to 9 mm<sup>2</sup>/s, in the range of from 4 to 8 mm<sup>2</sup>/s, or in the range of from 4.5 to 7.5 mm<sup>2</sup>/s. The kinematic viscosity may be measured according to ASTM D445.

According to the US Federal Register Vol. 78, no.112 Tuesday June 11 p 34867 7  
30 CFR Part 3201 final rule for example 3201.102, engine crankcase oil (that is lubricating compositions suitable for lubricating internal combustion engine crankcases) may be designated with a biopreferred ecolabel if they contain at least 25 % by weight biobased

carbon and water turbine bearing oils may be designated with a biopreferred ecolabel if they contain at least 46 % by weight biobased carbon.

In at least some examples the lubricating composition contains at least 25% by weight biobased carbon, for example at least 32 % by weight biobased carbon or at least 46 % by weight biobased carbon. In at least some examples the lubricating composition is a crankcase lubricating oil and contains at least 25 % by weight biobased carbon. In at least some examples the lubricating composition is a water turbine bearing oil and contains at least 46 % by weight biobased carbon. Methods of measuring biobased carbon content include those described in US Federal Register Vol. 78, no.112 Tuesday June 11 p 34867 7 CFR Part 3201 final rule including for example 3201.102, including for example as specified in the applicable section of subpart B of part 2902 and as defined in ASTM Method D6866 "Standard Test Methods for Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectroscopy Analysis".

Suitable lubricant additives for the lubricating composition according to embodiments of the present invention include detergents (including metallic and non-metallic detergents), friction modifiers, dispersants (including metallic and non-metallic dispersants), viscosity modifiers, dispersant viscosity modifiers, viscosity index improvers, pour point depressants, anti-wear additives, rust inhibitors, corrosion inhibitors, antioxidants (sometimes also called oxidation inhibitors), anti-foams (sometimes also called anti-foaming agents), seal swell agents (sometimes also called seal compatibility agents), extreme pressure additives (including metallic, non-metallic, phosphorus containing, non-phosphorus containing, sulphur containing and non-sulphur containing extreme pressure additives), surfactants, demulsifiers, anti-seizure agents, wax modifiers, lubricity agents, anti-staining agents, chromophoric agents, metal deactivators, and mixtures of two or more thereof.

In at least some examples, the at least one lubricant additive includes at least one detergent. Examples of detergents include ashless detergents (that is, non-metal containing detergents) and metal-containing detergents. Suitable non-metallic detergents are described for example in US 7,622,431. Metal-containing detergents comprise at least one metal salt of at least one organic acid, which is called soap or surfactant. The metals of the salts may be alkali metals, alkaline earth metals and combinations thereof. For example, the metals are calcium, magnesium and combinations thereof. Calcium and magnesium

detergent salts may both be present in the lubricating oil composition. Suitable metals  
detergents are neutral and over-based salts a TBN (total base number as measured by  
ASTM D2896) in the range about 20 to about 450. Suitable calcium sulfonates may have  
TBN (total base number) values of about 85, about 300 and about 400. Suitable calcium  
phenates may have TBN values of about 150 and about 250. Suitable calcium salicylate  
may have a TBN values of about 150 and about 300. Suitable organic acids include for  
example, sulphonic acids, phenols (suitably sulphurised and including for example,  
phenols with more than one hydroxyl group, phenols with fused aromatic rings, phenols  
which have been modified for example, alkylene bridged phenols, and Mannich base-  
condensed phenols and saligenin-type phenols, produced for example by reaction of phenol  
and an aldehyde under basic conditions) and sulphurised derivatives thereof, and  
carboxylic acids including for example, aromatic carboxylic acids (for example  
hydrocarbyl-substituted salicylic acids and derivatives thereof, for example hydrocarbyl  
substituted salicylic acids and sulphurised derivatives thereof). The at least one detergents  
may be present in the lubricating oil composition in a total amount of about 0.5 to about 12  
% by weight of the composition, for example about 1 to 3 % by weight of the composition.

In at least some examples, the at least one lubricant additive includes at least one  
friction modifier. Suitable friction modifiers include for example, ash-producing additives  
and ashless additives. Examples of suitable friction modifiers include fatty acid  
derivatives including for example, fatty acid esters, amides, amines, and ethoxylated  
amines. Examples of suitable ester friction modifiers include esters of glycerol for  
example, mono-, di-, and tri-oleates, mono-palmitates and mono-myristates. A particularly  
suitable fatty acid ester friction modifier is glycerol monooleate. Examples of suitable  
friction modifiers also include molybdenum compounds for example, organo molybdenum  
compounds, molybdenum dialkyldithiocarbamates, molybdenum dialkylthiophosphates,  
molybdenum disulphide, tri-molybdenum cluster dialkyldithiocarbamates, non-sulphur  
molybdenum compounds and the like. Suitable molybdenum-containing compounds are  
described for example, in EP 1533362 A1 for example in paragraphs [0101] to [0117]. The  
at least one friction modifier may be present in the lubricating oil composition in a total  
amount of less than about 1 % by weight of the composition, for example about 0.05 to  
about 0.8 % by weight.

In at least some examples, the at least one lubricant additive includes at least one dispersant. Each dispersant comprises one or more, for example at least two, oil soluble polymeric hydrocarbon backbones, each having one or more functional groups which are capable of associating with particles to be dispersed. The functional groups may be amine, alcohol, amide, or ester groups. Examples of suitable ashless dispersants include oil soluble salts, esters, amino-esters, amides, imides and oxazolines of long chain hydrocarbon-substituted mono- and polycarboxylic acids or anhydrides thereof; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons containing polyamine moieties attached directly thereto; Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine; Koch reaction products and the like. Preferred dispersants are polyisobutenyl succinimide dispersants. Suitable dispersants may be provided in one or more additive concentrates which may be used to provide a total active dispersant concentration of about 2.1 % by weight in the lubricating oil composition. The at least one dispersant may be present in the lubricating oil composition in a total amount of active dispersants of from about 1.5 to about 8 % by weight of the lubricating oil composition, for example in a total amount of active dispersants of from about 2 to about 2.5 % by weight of the lubricating oil composition.

In at least some examples, the at least one lubricant additive includes at least one dispersant viscosity modifiers. Each dispersant viscosity modifier may comprise more than one oil soluble, polymeric hydrocarbon backbone each having one or more functional groups which are capable of associating with particles to be dispersed. Each functionalised polymeric hydrocarbon backbone may be functionalised with one or more functional groups incorporated into the backbone or with one or more functional groups pendant from the polymer backbone. Typical functional groups may be polar and may contain one or more hetero atoms, for example phosphorus, oxygen, sulphur, nitrogen, halogen or boron. An example of a suitable dispersant viscosity modifier is a co-polymer of ethylene-propylene grafted with an active monomer, for example maleic anhydride and then derivatized with an alcohol or amine. The preparation of such dispersant viscosity modifiers is described for example in US 4,089,794, US 4,160,739 and US 4,137,185.

Other dispersant viscosity modifiers which may be used are copolymers of ethylene or propylene reacted or grafted with nitrogen compounds, for example as described in US

4,068,056, US 4,068,058, US 4,146,489 and US 4,149,984. Other dispersant viscosity modifiers which may be used are graft copolymers, for example as described in WO 96/12746 and WO 99/21902. The one or more dispersant viscosity modifiers may be used with one or more surfactants. These may stabilise the dispersant.

5 In at least some examples, the at least one lubricant additive includes at least one viscosity index improver. Examples of suitable viscosity modifiers include high molecular weight hydrocarbon polymers (for example polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins); polyesters (for example polymethacrylates); hydrogenated poly(styrene-co-butadiene or isoprene) polymers and modifications (for  
10 example star polymers); and esterified poly(styrene-co-maleic anhydride) polymers. Oil-soluble viscosity modifying polymers generally exhibit number average molecular weights of at least about 15,000 to about 1,000,000, for example about 20,000 to about 600,000, as determined by gel permeation chromatography or light scattering methods.

In at least some examples, the at least one lubricant additive includes at least one  
15 pour point depressant. Examples of suitable pour point depressants include C<sub>8</sub> to C<sub>18</sub> dialkyl fumarate/vinyl acetate copolymers, methacrylates, alkyl methacrylates, polyacrylates, polyarylamides, polymethacrylates, polyalkyl methacrylates, vinyl fumarates, styrene esters, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylate polymers, terpolymers of dialkylfumarates, vinyl esters of  
20 fatty acids and allyl vinyl ethers, wax naphthalene and the like. The at least one pour point depressants may be present in the lubricating oil composition in a total amount of up to 1 % by weight of the lubricating oil composition, for example in a total amount of about 0.05 to about 0.8 % by weight.

In at least some examples, the at least one lubricant additive includes at least one  
25 anti-wear additive. Examples of suitable anti-wear additives include non-phosphorus containing additives for example, sulphurised olefins. Examples of suitable anti-wear additives also include phosphorus-containing antiwear additives. Examples of suitable ashless phosphorus-containing anti-wear additives include trilauryl phosphite and triphenylphosphorothionate and those disclosed in paragraph [0036] of US 2005/0198894.  
30 Examples of suitable ash-forming, phosphorus-containing anti-wear additives include dihydrocarbyl dithiophosphate metal salts. Examples of suitable metals of the dihydrocarbyl dithiophosphate metal salts include alkali and alkaline earth metals,

aluminium, lead, tin, molybdenum, manganese, nickel, copper and zinc. Particularly suitable dihydrocarbyl dithiophosphate metal salts are zinc dihydrocarbyl dithiophosphates (ZDDP). Primary and/or secondary hydrocarbyl groups may be present in these compounds. Each hydrocarbyl group may have 1 to 18 carbon atoms. The at least one anti-  
5 wear additive may be present in the lubricating oil composition in a total amount of about 100 ppm to about 1,000 ppm by weight of the composition, for example about 250 to 800 ppm by weight of the composition.

In at least some examples, the at least one lubricant additive includes at least one rust inhibitor. Examples of suitable rust inhibitors include non-ionic polyoxyalkylene polyols  
10 and esters thereof, polyoxyalkylene phenols, polyoxyalkylene polyols, anionic alkyl sulphonic acids, zinc dithiophosphates, metal phenolates, basic metal sulphonates, fatty acids and amines.

In at least some examples, the at least one lubricant additive includes at least one corrosion inhibitor. Examples of corrosion inhibitors non-ionic polyoxyalkylene polyols  
15 and esters thereof, polyoxyalkylene phenols, thiadiazoles, triazoles, anionic alkyl sulphonic acids, and phosphosulphurised hydrocarbons and the products obtained by the reaction of phosphosulphurised hydrocarbon with an alkaline earth metal oxide or hydroxide.

Examples of suitable epoxidised ester corrosion inhibitors are described in US 2006/0090393. The at least one corrosion inhibitors may be present in the lubricating oil  
20 composition in a total amount of up to about 1 % by weight of the lubricating oil composition, for example in a total amount of about 0.05 to about 0.8 % by weight of the lubricating oil composition.

In at least some examples, the at least one lubricant additive includes at least one antioxidant. Examples of suitable antioxidants include alkylated diphenylamines, N-  
25 alkylated phenylenediamines, phenyl- $\alpha$ -naphthylamine, alkylated phenyl- $\alpha$ -naphthylamines, dimethylquinolines, trimethyldihydroquinolines and oligomeric compositions derived therefrom, hindered phenolics (including ashless (metal-free) phenolic compounds and neutral and basic metal salts of certain phenolic compounds), aromatic amines (including alkylated and non-alkylated aromatic amines), sulphurised  
30 alkyl phenols and alkali and alkaline earth metal salts thereof, alkylated hydroquinones, hydroxylated thiodiphenyl ethers, alkylidenebisphenols, thiopropionates, metallic dithiocarbamates, 1,3,4-dimercaptothiadiazole and derivatives, oil soluble copper

compounds (for example, copper dihydrocarbyl thio- or thio-phosphate, copper salts of a synthetic or natural carboxylic acids, for example a C<sub>8</sub> to C<sub>18</sub> fatty acid, an unsaturated acid or a branched carboxylic acid, for example basic, neutral or acidic Cu<sup>I</sup> and/or Cu<sup>II</sup> salts derived from alkenyl succinic acids or anhydrides), alkaline earth metal salts of

5 alkylphenolthioesters, suitably containing C<sub>5</sub> to C<sub>12</sub> alkyl side chains, calcium nonylphenol sulphide, barium *t*-octylphenyl sulphide, dioctylphenylamine, phosphosulphised or sulphurised hydrocarbons, oil soluble phenates, oil soluble sulphurised phenates, calcium dodecylphenol sulphide, phosphosulphurised hydrocarbons, sulphurised hydrocarbons, phosphorus esters, low sulphur peroxide decomposers and the like. The at least one anti-oxidants may be present in the lubricating oil composition in a total amount of up to about 10 5 % by weight of the lubricating oil composition, for example from about 1 to 3 % by weight of the lubricating oil composition.

In at least some examples, the at least one lubricant additive includes at least one antifoam. Examples of suitable anti-foam agents include silicones, organic polymers, 15 siloxanes (including poly siloxanes and (poly) dimethyl siloxanes, phenyl methyl siloxanes), acrylates and the like. The at least one anti-foaming agents may be present in the lubricating oil composition in a total amount by weight typically of about 10 to about 100 ppm of the lubricating oil composition, for example in a total amount by weight of about 25 to about 75 ppm of the lubricating oil composition

20 In at least some examples, the at least one lubricant additive includes at least one seal swell agent. Examples of suitable seal swell agents include long chain organic acids, organic phosphates, aromatic esters, aromatic hydrocarbons, esters (for example butylbenzyl phthalate) and polybutenyl succinic anhydride.

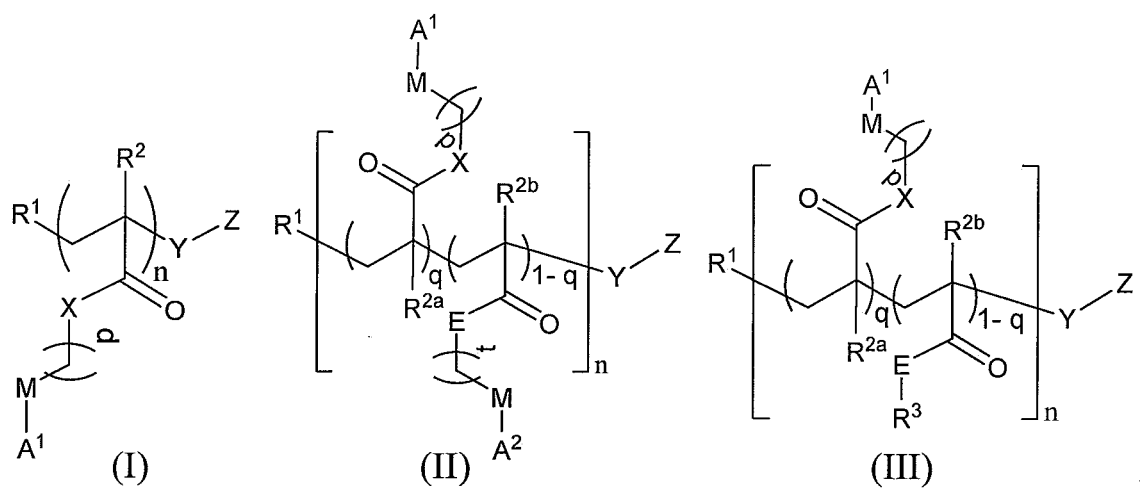
In another aspect, the present disclosure provides a method for lubricating an internal 25 combustion engine, such as two-stroke or four-stroke diesel engines, comprising supplying to said engine a lubricating composition as defined herein.

Suitable internal combustion engines include, for example, engines used in automotive applications, engines used in marine applications and engines used in land-based power generation plants.

30 In at least some examples, the lubricating composition of the invention is used to lubricate the crankcase of an internal combustion engine at any temperature which is typically encountered in an engine environment, for example a temperature in the range of

ambient to about 250 °C, e.g. about 90 to about 120 °C. Typically, ambient temperature is 20 °C, but according to at least some embodiments, ambient temperature is for example less than 20°C, for example 0°C.

In another aspect, the present disclosure also provides an amine-containing diblock copolymer according to Formula I, II and/or III below:



wherein R<sup>1</sup> to R<sup>3</sup>, A<sup>1</sup>, A<sup>2</sup>, M, E, X, Y, Z, n, t, p and q are as defined hereinbefore.

In a further aspect, the present disclosure provides a use of an amine-containing diblock copolymer according to Formula I, II and/or III as defined hereinbefore for increasing ashless TBN in a lubricating oil composition comprising a base oil of lubricating viscosity and one or more lubricant additives.

Embodiments of the present invention will now be illustrated by way of the following examples and with reference to the following figures:

Figure 1: Graph showing number weighted distribution of hydrodynamic diameter for a diblock copolymer according to Formula I of the invention (DMAEMA Mod) analysed by dynamic light scattering (DLS) in hexane;

Figure 2: Graph of pK<sub>a</sub> values for diblock copolymers according to Formula I of the invention (DMAEMA Mod) of various molecular weights (1, 2 and 85 kDa) compared with the corresponding non-end group modified polymers (DMAEMA RAFT).

Figure 3: Graph of pK<sub>a</sub> values for diblock copolymers according to Formula I of the invention (DEAEMA Mod) of various molecular weights (1, 2 and 85 kDa) compared with the corresponding non-end group modified polymers (DEAEMA RAFT).

Figure 4: Graph of  $pK_a$  values for diblock copolymers according to Formula I of the invention (PEMA Mod) of various molecular weights (1, 2 and 85 kDa) compared with the corresponding non-end group modified polymers (PEMA RAFT).

Figure 5: Graph of  $pK_a$  values for diblock copolymers according to Formula I of the invention (MEMA Mod) of various molecular weights (1, 2 and 85 kDa) compared with the corresponding non-end group modified polymers (MEMA RAFT).

Figure 6: Graph showing number weighted distribution of hydrodynamic diameter for a diblock copolymer according to Formula III of the invention (DMAEMA-co-LMA Mod) analysed by dynamic light scattering (DLS) in hexane;

Figure 7: Graph of  $pK_a$  values for diblock copolymers according to Formula III of the invention (DMAEMA-co-LMA Mod) of various percentage amine incorporation values and the corresponding non-end group modified polymers (DMAEMA-co-LMA RAFT);

Figure 8: Graph of  $pK_a$  values for diblock copolymers according to Formula III of the invention (DEAEMA-co-LMA Mod) of various percentage amine incorporation values and the corresponding non-end group modified polymers (DEAEMA-co-LMA RAFT);

Figure 9: Graph of  $pK_a$  values for diblock copolymers according to Formula III of the invention (MEMA-co-LMA Mod) of various percentage amine incorporation values and the corresponding non-end group modified polymers (MEMA-co-LMA RAFT);

The following examples are merely illustrative and shall not be interpreted as limiting the scope of protection as defined in the claims.

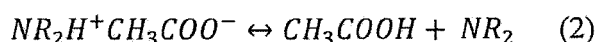
### Examples

#### General method for determination of $pK_a$

Potentiometric titration is performed at room temperature with an automatic titrator (Mettler Toledo G20) having a DGi115-SC pH sensor suitable for non-aqueous systems and the titration being controlled by LabX software. 30 mL of solution, with a concentration of amine-containing polymer corresponding to  $2.08 \times 10^{-6}$  M of ionisable groups, is used for each potentiometric titration experiment. Polymers are first dissolved in MeCN for 24 hrs before being titrated with glacial acetic acid. The glacial acetic acid titrant is added at volume increments of 0.1-5  $\mu$ L and at 180 s intervals. The observed change in pH is plotted as a function of the degree of ionization,  $\alpha$ , from which the total amount of titrable amine units is also calculated.

The degree of ionisation,  $\alpha$ , is defined by Equation (1) below and the equilibrium that exists between the ionisable groups in solution and the acidic protons from acetic acid according to Equation (2).

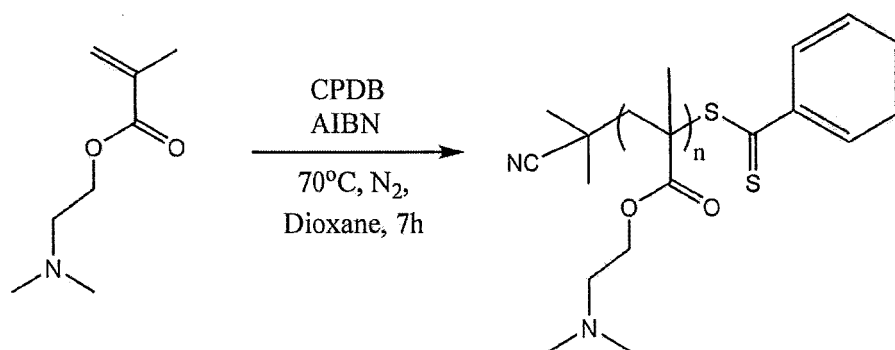
$$\alpha = \frac{[NR_2H^+CH_3COO^-]}{[NR_{2total}]} \quad (1)$$



For complete protonation of amine units,  $\alpha = 1$  and for complete deprotonation of amine units,  $\alpha = 0$ .  $[NR_{2total}]$  is determined on the basis of the amine-containing polymer tested, understanding that each amine repeat unit along the polymer chain can be ionised.  $[NR_{2total}]$  corresponds to the concentration of all the amine in the system, calculated from the mass of the polymer added to the solution. The  $pK_a$  is determined on the basis that the pH value when  $\alpha = 0.5$  is the  $pK_a$  value.

### Example 1

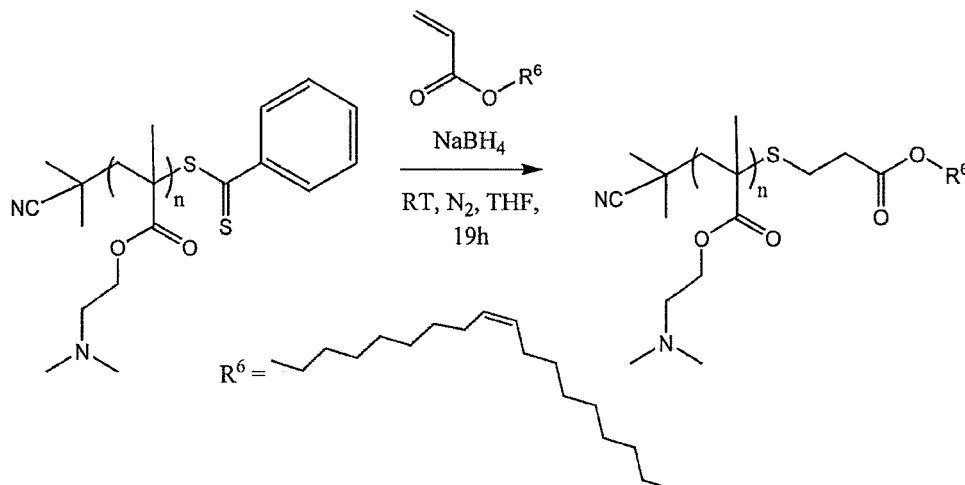
#### Homopolymerization of dimethylaminoethyl methacrylate (DMAEMA)



A solution of 6 equivalents of DMAEMA, 0.2 equivalents of AIBN and 1 equivalent of 2-cyano-2-propyl dithiobenzoate (CPDB) in 1,4-dioxane (1:1 volume compared to monomer) was added to a dry ampule containing a stirrer bar. The solution was degassed using at least 3 freeze-pump-thaw cycles, back filled with nitrogen, sealed and placed in a pre-heated oil bath at 70 °C. After 7 hours the polymerization was quenched by liquid nitrogen, the dioxane removed in vacuo and the resultant polymer diluted with water. The solution was transferred to a dialysis membrane tube with the appropriate molecular weight cut-off and dialyzed against water with three water changes. Lyophilization afforded the

dithioester terminated homopolymer in a form suitable for subsequent end-group modification.

### End-group modification of DMAEMA RAFT product with oleyl acrylate



1 equivalent of DMAEMA RAFT homopolymer, 50 equivalents of oleyl acrylate and 50 equivalents of THF were transferred to an ampule. The mixture was degassed before sodium borohydride (20 equivalents) and tributyl phosphine (10 equivalents) were added. The ampule was sealed under nitrogen and stirred at room temperature for 19 hours. The mixture obtained was passed through a flash silica column with dichloromethane : methanol 10:1 to give the desired diblock copolymer product (DMAEMA Mod) illustrated above.

The diblock copolymer product was characterised by size exclusion chromatography and by  $^1\text{H}$  NMR. Micelle formation was verified in hexane using dynamic light scattering (DLS), the results of which are shown in Figure 1. Heptane may also be used as a solvent for micelle formation. Figure 1 shows a micelle hydrodynamic diameter of approximately 10 nm, which is significantly larger than the corresponding single non-assembled polymer chain, which would be expected to have a hydrodynamic diameter of between 2 and 4 nm.

### Example 2

20 The method of Example 1 was repeated except an increased ratio of monomer to chain transfer agent was used and the time period over which the reaction was conducted was adjusted where necessary in order to increase the number of repeat monomer units (n) of the dithioester terminated RAFT polymer and thereby increase the molecular weight of

the diblock copolymer obtained. Where a larger polymer of, for instance, 85 kDa was desired, the reaction time was extended up to 18 hours.

The method of Example 1 was also employed for different monomers (diethylaminoethyl methacrylate (DEAEMA), 2-N-morpholinoethyl methacrylate (MEMA), and 4-pyridylethyl methacrylate (PEMA)) with different n repeat units to give different molecular weight diblock copolymers. The same end-group modification using oleyl acrylate was subsequently used in each case.

The BN (mg KOH/g),  $pK_a$  (MeCN) and theoretical nitrogen content (mol %) of the monomers and their corresponding diblock copolymer (based on the molecular weight) were determined and results are provided in Table 1 below. BN values were measured according to ASTM D2896.  $pK_a$  values were determined using the general method described herein before. "Mod" in Table 1 below refers to the end-group modified diblock copolymer product. "RAFT" refers to the dithioester terminated polymer, prior to modification.

Table 1

| Amine Functionality | Polymer     | Molecular Wt (kDa) | N mol% | $pK_a$ (MeCN) | BN (mg KOH/g) |
|---------------------|-------------|--------------------|--------|---------------|---------------|
| Dimethyl amine      | DMAEMA Mod  | 1                  | 7.8    | 7.9           | 320           |
|                     | DMAEMA RAFT | 1                  | 8.4    | 7.6           | 192           |
|                     | DMAEMA Mod  | 2                  | 8.3    | 10.3          | 274           |
|                     | DMAEMA RAFT | 2                  | 8.7    | 10.0          | 265           |
|                     | DMAEMA Mod  | 85                 | 8.9    | 8.3           | 210           |
|                     | DMAEMA RAFT | 85                 | 8.9    | 8.0           | 193           |
|                     |             |                    |        |               |               |
| Diethyl amine       | DEAEMA Mod  | 1                  | 6.8    | 10.5          | 122           |
|                     | DEAEMA RAFT | 1                  | 7.3    | 9.8           | 234           |
|                     | DEAEMA Mod  | 2                  | 7.2    | 11.2          | 313           |
|                     | DEAEMA RAFT | 2                  | 7.5    | 10.1          | 267           |
|                     | DEAEMA Mod  | 85                 | 7.6    | 10.2          | 399           |
|                     | DEAEMA RAFT | 85                 | 7.6    | 9.7           | 68            |
|                     |             |                    |        |               |               |
| Morpholinyl         | MEMA Mod    | 1                  | 6.4    | 5.0           | 374           |
|                     | MEMA RAFT   | 1                  | 6.9    | 4.8           | 147           |
|                     | MEMA Mod    | 2                  | 6.7    | 6.5           | 239           |
|                     | MEMA RAFT   | 2                  | 7.0    | 5.1           | 220           |
|                     | MEMA Mod    | 85                 | 7.0    | 8.0           | 172           |
|                     | MEMA RAFT   | 85                 | 7.0    | 8.0           | 274           |

| <b>Pyridyl</b> | PEMA Mod  | 1  | 6.6 | <b>9.2</b> | 283 |
|----------------|-----------|----|-----|------------|-----|
|                | PEMA RAFT | 1  | 7.2 | <b>8.9</b> | 124 |
|                | PEMA Mod  | 2  | 7.0 | <b>9.3</b> | 127 |
|                | PEMA RAFT | 2  | 7.2 | <b>9.1</b> | 128 |
|                | PEMA Mod  | 85 | 7.3 | <b>9.5</b> | -   |
|                | PEMA RAFT | 85 | 7.3 | <b>9.2</b> | -   |

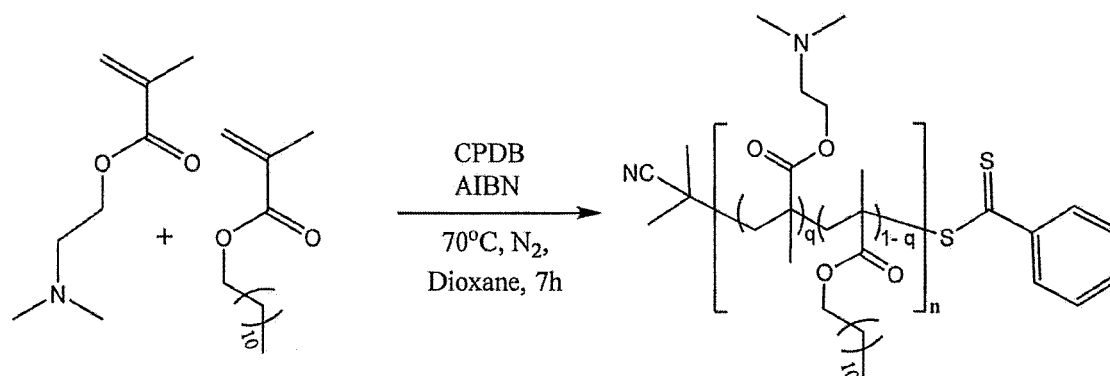
The results of Table 1 are represented graphically in Figures 2 to 5. These results illustrate the surprising effects of embodiments of the present invention.  $pK_a$  values for the diblock copolymer according to the invention are appreciably higher than for the corresponding non-modified dithioester terminated RAFT polymer derivatives. This is despite a lower mol % of nitrogen in the diblock copolymer. These results demonstrate the benefit of reverse micelle formation occurring with the diblock copolymers according to the present invention.

The reverse micelle assembly positions the polar amine-containing block of the amphiphilic diblock copolymer towards the centre of the micelle assembly, thereby forming a dense polar core. As a result of cooperative basicity effects in the core of the micelle, the strength of the base is increased, as illustrated by an increase in  $pK_a$  value, in comparison to the corresponding non-modified RAFT polymer derivatives, which do not form micelles.

The results in Table 1 also demonstrate that the diblock copolymers according to the invention correspond to sources of significant TBN and may therefore be considered as ashless TBN boosters. The results in Table 1 also illustrate a general trend in which TBN values observed for the diblock copolymers according to the invention are increased over the corresponding non-modified RAFT polymer derivatives. Without being bound by any particular theory, the general increase in TBN value observed following micelle formation is believed to be a result of the improved accessibility of the basic amine groups in the core of the micelle for neutralising acids. Exceptions to this general trend are believed to be a result of a lack of suitability of the standard method employed in determining TBN.  $pK_a$  results consistently illustrate an increase in basicity as a result of micelle formation and are considered to be a more reliable representation of the effects of the invention related to the affinity of the Formulae I, II and III towards acids, as discussed hereinbefore.

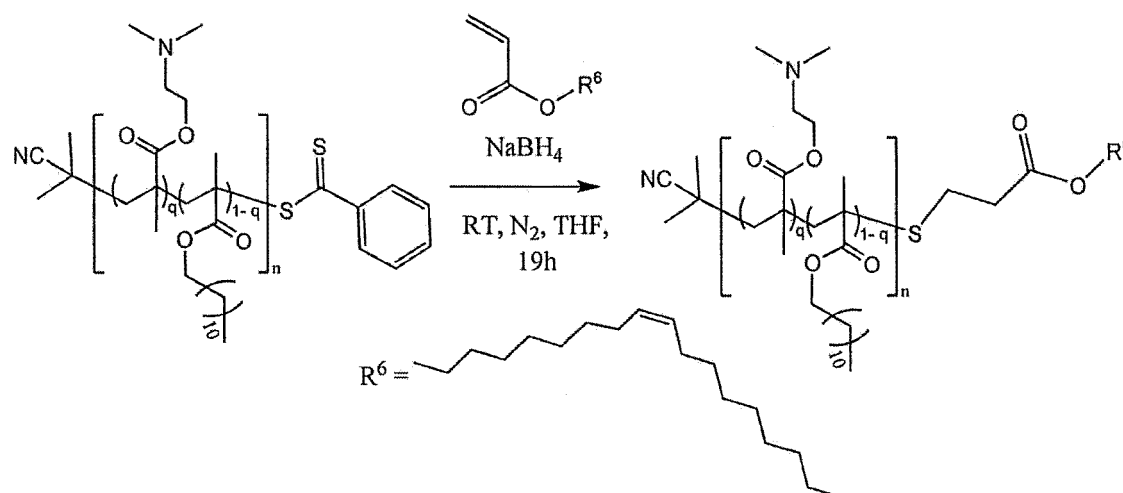
### Example 3

Co-polymerisation of dimethylaminoethyl methacrylate (DMAEMA) with lauryl methacrylate (LMA)



- 5 A solution of 12 equivalents of DMAEMA, 3 equivalents of LMA, 0.2 equivalents of AIBN and 1 equivalent of 2-cyano-2-propyl dithiobenzoate (CPDB) in 1,4-dioxane (1:1 volume compared to monomer) was added to a dry ampule containing a stirrer bar. The solution was degassed using at least 3 freeze-pump-thaw cycles, back filled with nitrogen, sealed and placed in a pre-heated oil bath at 70 °C. After 7 hours the polymerization was  
10 quenched by liquid nitrogen, the dioxane removed *in vacuo* and the resultant polymer diluted with water. The solution was transferred to a dialysis membrane tube with the appropriate molecular weight cut-off and dialyzed against water with three water changes. Lyophilization afforded the dithioester terminated copolymer in a form suitable for subsequent end-group modification.

15 End-group modification of DMAEMA-co-LMA RAFT product with oleyl acrylate



A solution of 1 equivalent of DMAEMA-co-LMA RAFT polymer in THF, 50 equivalents of olely acrylate and 50 equivalents of THF were transferred to an ampule. The mixture was degassed before sodium borohydride (20 equivalents) and tributyl phosphine (10 equivalents) were added. The ampule was sealed under nitrogen and stirred at room  
5 temperature for 19 hours. The mixture was passed through a flash silica column with dichloromethane : methanol 10:1 to give the desired product diblock copolymer product.

The diblock copolymer product was characterised by size exclusion chromatography and by  $^1\text{H}$  NMR. Micelle formation was verified in hexane using dynamic light scattering (DLS), the results of which are shown in Figure 6. Figure 6 shows a micelle  
10 hydrodynamic diameter of approximately 10 nm, which is significantly larger than the corresponding single non-assembled polymer chain, which would be expected to have a hydrodynamic diameter of between 2 and 4 nm.

#### Example 4

The method of Example 3 was repeated except the number of equivalents of  
15 monomers was adjusted in order to alter the incorporation of amine units (n) of the dithioester terminated RAFT copolymer in order to vary the amine mol% of the diblock copolymer obtained. The method of Example 3 was also employed with different combinations of co-monomers (diethylaminoethyl methacrylate-co-lauryl methacrylate (DEAEMA-co-LMA), and 2-N-morpholinoethyl methacrylate-co-lauryl methacrylate  
20 (MEMA-co-LMA)) with different n repeat units to give different molecular weight diblock copolymers. The same end-group modification using olely acrylate was used in each case.

The TBN (mg KOH/g),  $pK_a$  (MeCN) and nitrogen content (mol%) of the end-group modified diblock copolymers were determined and results are provided in Table 2 below. Amine incorporation values (mol %) in the diblock copolymer are also provided in Table  
25 2, which are determined on the basis of the ratio of the two co-monomers used during RAFT polymerisation. TBN values were measured according to ASTM D2896.  $pK_a$  values were determined using the general method described hereinbefore. "Mod" recited in Table 2 refers to the end-group modified diblock copolymer product whilst "RAFT" refers to the dithioester terminated polymer prior to modification.

Table 2

| Polymer            | % Amine incorporation | % Alkyl Co-monomer | MW (kDa) | N mol % | TBN (mg KOH/g) | pK <sub>a</sub> (MeCN) |
|--------------------|-----------------------|--------------------|----------|---------|----------------|------------------------|
| DMAEMA-co-LMA RAFT | 25                    | 75                 | 3.5      | 2.2     | 41             | 8.0                    |
| DMAEMA-co-LMA RAFT | 50                    | 50                 | 3.2      | 4.5     | 105            | 7.8                    |
| DMAEMA-co-LMA RAFT | 75                    | 25                 | 4.2      | 6.7     | 126            | 7.6                    |
|                    |                       |                    |          |         |                |                        |
| DMAEMA-co-LMA MOD  | 25                    | 75                 | 3.6      | 2.2     | 61             | 8.2                    |
| DMAEMA-co-LMA MOD  | 50                    | 50                 | 3.5      | 4.4     | 102            | 8.0                    |
| DMAEMA-co-LMA MOD  | 75                    | 25                 | 4.2      | 6.6     | 149            | 8.0                    |
|                    |                       |                    |          |         |                |                        |
| DEAEMA-co-LMA RAFT | 25                    | 75                 | 2.1      | 2.2     | 49             | 8.9                    |
| DEAEMA-co-LMA RAFT | 50                    | 50                 | 2.3      | 4.4     | 89             | 8.6                    |
| DEAEMA-co-LMA RAFT | 75                    | 25                 | 2.3      | 6.7     | 140            | 8.1                    |
|                    |                       |                    |          |         |                |                        |
| DEAEMA-co-LMA MOD  | 25                    | 75                 | 2.2      | 2.2     | 33             | 9.7                    |
| DEAEMA-co-LMA MOD  | 50                    | 50                 | 2.3      | 4.4     | 70             | 9.4                    |
| DEAEMA-co-LMA MOD  | 75                    | 25                 | 2.3      | 6.6     | 101            | 9.3                    |
|                    |                       |                    |          |         |                |                        |
| MEMA-co-LMA RAFT   | 25                    | 75                 | 3.2      | 1.8     | 66.3           | 5.2                    |
| MEMA-co-LMA RAFT   | 50                    | 50                 | 2.9      | 3.5     | 133.8          | 5.2                    |
| MEMA-co-LMA RAFT   | 75                    | 25                 | 3.3      | 5.3     | 112.0          | 5.1                    |
|                    |                       |                    |          |         |                |                        |
| MEMA-co-LMA MOD    | 25                    | 75                 | 3.4      | 1.7     | 66.8           | 6.8                    |
| MEMA-co-LMA MOD    | 50                    | 50                 | 3.1      | 3.3     | 119.4          | 6.8                    |
| MEMA-co-LMA MOD    | 75                    | 25                 | 3.5      | 4.9     | 197.4          | 6.6                    |

The results of Table 2 are represented graphically in Figures 7 to 9. These results illustrate the surprising effects of the invention. The amine-containing diblock copolymers according to the invention have higher  $pK_a$  values than the corresponding non end group modified RAFT derivatives, as a result of increased cooperative basicity upon micelle formation.

Figures 7 to 9 also demonstrates that lower amine incorporation in the polar block gives higher  $pK_a$  values. By copolymerising with a hydrophobic group (in this case LMA), the amine groups become more spaced out along the polymer chain. As a result, charge proximity issues between proximal amine groups, as well as steric hindrance issues between amine groups of adjacent polymer chains, are mitigated. Consequently, the basicity of individual amine groups is increased leading to increased  $pK_a$  values.

The results in Table 2 also demonstrate that the diblock copolymers described hereinbefore correspond to sources of significant BN and may therefore be considered as ashless TBN boosters. A general trend is also observed with the BN results in Table 2 where BN values increase with increasing levels of amine incorporation in the polar block, both in the diblock copolymer of the invention and the corresponding non end group modified RAFT derivative. This is because there is an increased population of basic amine groups contributing to BN.

#### Example 5

Compositions (A to C) were prepared with a majority of a commercial Group I base oil (SN 600 available from Shamrock), together with either: A) DEAEMA-co-LMA modified with oleyl acrylate (BN = 101 mg of KOH/g, %N = 2.2); B) a commercial ashless succinimide dispersant (PIBSA-PAM) with a TBN value of 75 mg of KOH/g; or C) a commercial ashless succinimide dispersant (PIBSA-PAM) with a TBN value of 29 mg of KOH/g. TBN values for the compositions were measured for each composition according to the standard methods indicated. Results are provided in Table 3 below.

Table 3

| Components        | % wt/wt in oil composition |       |       |
|-------------------|----------------------------|-------|-------|
|                   | A                          | B     | C     |
| Base Oil          | 95                         | 92.86 | 82.76 |
| DEAEMA-co-LMA mod | 5                          | 0     | 0     |
| PIBSA-PAM, 75 TBN | 0                          | 7.14  | 0     |
| PIBSA-PAM, 29 TBN | 0                          | 0     | 17.24 |
| BN ashless        | 5                          | -     | -     |
| % nitrogen        | 0.38                       | -     | -     |
|                   |                            |       |       |
| TBN (D2896)       | 5.35                       | 5.46  | 5.04  |
| TBN (D4739)       | 5.13                       | 4.11  | 3.51  |

The results of Table 3 illustrate the advantages of the invention. The TBN values measured for the different compositions highlight that the amine-containing diblock copolymer of the invention delivers a higher amount of TBN per unit weight in comparison to commercial ashless succinimide dispersants. For instance, a treat rate of only 5 wt.% of the amine-containing diblock copolymer of the invention delivers a similar or higher TBN value than is provided by the commercial ashless succinimide dispersants used in higher concentrations.

#### Example 6

A fully formulated engine oil composition (D) was prepared comprising a commercial additive package including overbased detergents (contributing a TBN of 18 mg KOH/g) and dispersants, all of which being suitable for marine cylinder lubricant applications, together with an amount of DEAEMA-co-LMA modified with oleyl acrylate (BN = 101 mg KOH/g, %N = 2.2) and the balance being a commercial Group I base oil (SN 600 available from Shamrock). TBN values for the formulated oil were measured according to ASTM D2896. Kinematic viscosity values for the formulated oils were determined in accordance with ASTM D445 whilst viscosity index values were determined in accordance with ASTM D2270. Results are provided in Table 4 below.

Table 4

|                   | wt/wt % in fully formulated oil |
|-------------------|---------------------------------|
| <b>Components</b> | <b>D</b>                        |
| Additive package  | 17.7                            |
| DEAEMA-co-LMA Mod | 5                               |
| Total Additives   | 22.7                            |
|                   |                                 |
| TBN               | 23                              |
| KV 100            | 20.53                           |
| KV 40             | 238.8                           |
| VI                | 100                             |

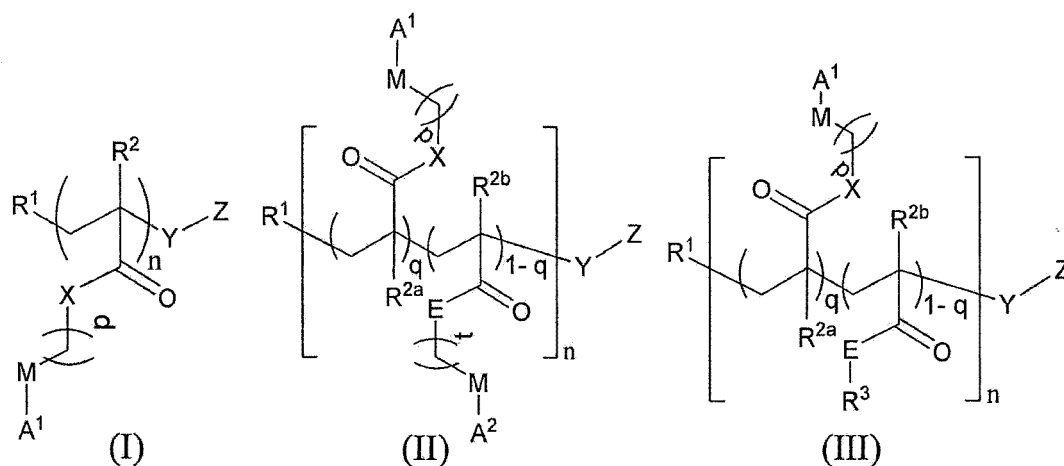
The results of Table 4 illustrate that a fully formulated lubricating composition comprising the amphiphilic diblock copolymer in accordance with the invention can readily be prepared and with suitable dynamic viscosity and viscosity index values.

- 5 Furthermore, TBN results also demonstrate that the diblock copolymer according to the invention is capable of acting as an ashless TBN booster. The overbased detergents of the additive package in the oil contribute a TBN of 18 mg KOH/g. However, the measured TBN of the fully formulated oil, including the ashless TBN contributed by the diblock copolymer according to the invention, is 23 mg KOH/g. This demonstrates that the
- 10 presence of the diblock copolymer according to the invention does not have a deleterious effect on the TBN contributed by the overbased detergents but contributes additional, ashless TBN, on which basis the diblock copolymer can be considered an ashless TBN booster.

**Claims**

1. A lubricating composition comprising a base oil of lubricating viscosity, one or more lubricant additives and an ashless TBN booster selected from an amine-containing diblock copolymer according to Formula I, II and/or III below:

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wherein:

$R^1$  is a  $C_1$  to  $C_{12}$  straight chain or branched alkyl group, a  $C_6$  to  $C_{10}$  aryl group or a 3 to 10 membered heterocyclic group, wherein said alkyl, aryl or heterocyclic groups may be unsubstituted or substituted;

$R^2$ ,  $R^{2a}$  and  $R^{2b}$  are independently H or methyl;

$R^3$  is a  $C_1$ - $C_{24}$  straight chain or branched alkyl group;

E is O or NH;

X is O or NH;

Y is S, S(=O), or S(=O)<sub>2</sub>;

Z is selected from:

$-\text{CH}_2\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{R}^6$ ,  $\text{CH}_2\text{CH}_2-\text{C}(=\text{O})-\text{R}^6$ ,  $-\text{CH}_2\text{CH}_2-\text{C}(=\text{O})-\text{S}-\text{R}^6$ ,

$-\text{CH}_2\text{CH}_2-\text{C}(=\text{O})-\text{NH}-\text{R}^6$ ,  $-\text{CH}_2\text{CH}_2-\text{C}(=\text{S})-\text{NH}-\text{R}^6$ , and

$-\text{CH}(-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{R}^6)(-\text{C}(=\text{O})-\text{O}-\text{R}^6)$ ;

$R^6$  is a  $C_6$  to  $C_{50}$  aliphatic hydrocarbyl group;

M is  $\text{CH}_2$ ;

$A^1$  and  $A^2$  are independently selected from  $-\text{NR}^4\text{R}^5$ , a 3 to 10 membered heterocyclic group containing a nitrogen ring atom which is not attached to M via a nitrogen

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atom, or a C<sub>6</sub> to C<sub>10</sub> aryl group substituted by 1 to 2 -NR<sub>j</sub>R<sub>k</sub> groups; provided that when X and E are the same and R<sup>2a</sup> and R<sup>2b</sup> are the same, A<sup>1</sup> and A<sup>2</sup> are different; R<sup>4</sup> and R<sup>5</sup> are independently selected from hydrogen, a C<sub>1</sub> to C<sub>8</sub> straight chain or branched alkyl group, a C<sub>2</sub> to C<sub>8</sub> straight chain or branched alkenyl group, a C<sub>3</sub> to C<sub>8</sub> cycloalkyl group, a C<sub>6</sub> to C<sub>10</sub> aryl group and a 3 to 10 membered heterocyclic group; or R<sub>4</sub> and R<sub>5</sub> together with the nitrogen atom to which they are attached combine to form a 3 to 10 membered heterocyclic group, wherein said alkyl, alkenyl, cycloalkyl, aryl and heterocyclic groups are unsubstituted or may be substituted by one to three groups selected from: C<sub>1</sub> to C<sub>6</sub> alkoxy, C<sub>2</sub> to C<sub>8</sub> alkoxyalkoxy, C<sub>3</sub> to C<sub>8</sub> cycloalkyl, C<sub>6</sub> to C<sub>10</sub> aryl, 3 to 10 membered heterocyclic, C<sub>7</sub> to C<sub>10</sub> aralkyl, 3 to 10 membered heterocyclic-C<sub>1</sub> to C<sub>4</sub> alkyl, -OH, or -NR<sub>j</sub>R<sub>k</sub>; R<sub>j</sub> and R<sub>k</sub> are independently selected from C<sub>1</sub> to C<sub>6</sub> straight chain or branched alkyl group;

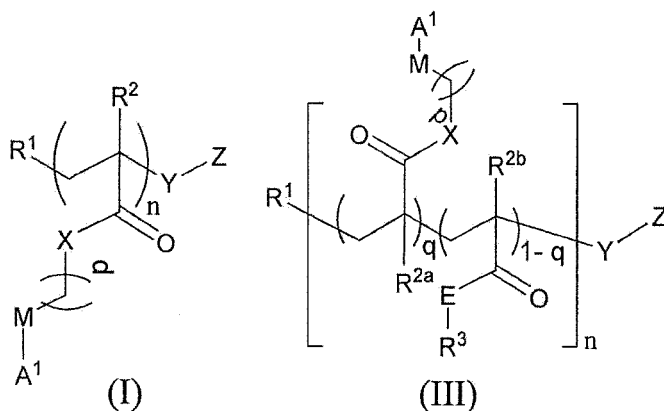
n is an integer from 5 to 500;

p is an integer from 1 to 12;

t is an integer from 1 to 12; and

q is greater than zero but less than 1.

2. A lubricating composition according Claim 1, wherein the composition comprises an ashless TBN booster selected from an amine-containing diblock copolymer according to Formula I and/or III below:



wherein R<sup>1</sup> to R<sup>3</sup>, A<sup>1</sup>, M, E, X, Y, Z, n, t, p and q are as defined in Claim 1.

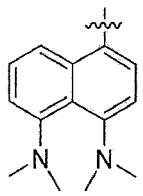
3. A lubricating composition according to Claim 1 or Claim 2, wherein  $R^1$  is unsubstituted or substituted by one to three groups selected from: -CN, -OH, -SH, -NO<sub>2</sub>, -CO<sub>2</sub>R<sup>x</sup>, -OC(O)R<sup>x</sup>, -C(O)R<sup>x</sup>, C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>6</sub> to C<sub>10</sub> aryl, 3 to 10 membered heterocyclic, C<sub>7</sub> to C<sub>10</sub> aralkyl, and 3 to 10 membered heterocyclic-C<sub>1</sub> to C<sub>4</sub> alkyl, wherein R<sup>x</sup> is selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl.
4. A lubricating composition according to Claim 3, wherein  $R^1$  is unsubstituted or substituted by one to three groups selected from: -CN, -OH, -SH, -NO<sub>2</sub>, -CO<sub>2</sub>R<sup>x</sup>, and -OC(O)R<sup>x</sup>, wherein R<sup>x</sup> is selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl; preferably wherein when  $R^1$  is unsubstituted or substituted by one to three groups selected from: -CN, -CO<sub>2</sub>R<sup>x</sup>, and -OC(O)R<sup>x</sup>, wherein R<sup>x</sup> is selected from hydrogen or C<sub>1</sub> to C<sub>6</sub> alkyl; for example wherein  $R^1$  is unsubstituted or substituted by a single -CN group.
5. A lubricating composition according any of Claims 1 to 3, wherein  $R^1$  is a C<sub>1</sub> to C<sub>6</sub> straight chain or branched alkyl group; preferably wherein  $R^1$  is a C<sub>3</sub> to C<sub>6</sub> branched alkyl group, for example wherein  $R^1$  is -CH(CH<sub>2</sub>)<sub>2</sub>CN.
6. A lubricating composition according to any of the preceding claims, wherein R<sup>2</sup>, R<sup>2a</sup> and/or R<sup>2b</sup> is methyl.
7. A lubricating composition according to any of the preceding claims, wherein A<sup>1</sup> and/or A<sup>2</sup> as applicable is/are -NR<sup>4</sup>R<sup>5</sup>.
8. A lubricating composition according to Claim 7, wherein R<sup>4</sup> and R<sup>5</sup> are independently selected from a C<sub>1</sub> to C<sub>4</sub> straight chain or branched alkyl group, preferably wherein R<sup>4</sup> and R<sup>5</sup> are both a methyl or ethyl group; or wherein R<sup>4</sup> and R<sup>5</sup> together with the nitrogen atom to which they are attached combine to form a 3 to 10 membered heterocyclic group, for example a morpholinyl group.
9. A lubricating composition according to any of Claims 1 to 6, wherein A<sup>1</sup> and/or A<sup>2</sup> as applicable is/are a 3 to 10 membered heterocyclic group containing a nitrogen ring

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atom which is not attached to M via a nitrogen atom, for example wherein the heterocyclic group is morpholinyl or pyridyl.

10. A lubricating composition according to any of Claims 1 to 6, wherein A<sup>1</sup> and/or A<sup>2</sup> as applicable is/are a C<sub>6</sub> to C<sub>10</sub> aryl group substituted by 1 to 2 -NR<sub>j</sub>R<sub>k</sub> groups, for



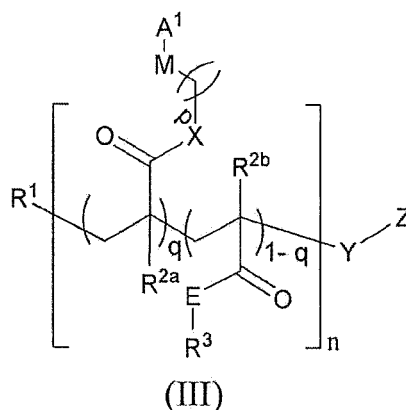
example, wherein the aryl group is:

11. A lubricating composition according to any of the preceding claims, wherein X is O, E is O, and/or Y is S.

12. A lubricating composition according to any of the preceding claims, wherein Z is selected from: -CH<sub>2</sub>CH<sub>2</sub>-C(=O)-O-R<sup>6</sup> and -CH(-CH<sub>2</sub>-C(=O)-O-R<sup>6</sup>)(-C(=O)-O-R<sup>6</sup>).

13. A lubricating composition according to any of the preceding claims, wherein R<sup>6</sup> is a C<sub>16</sub> to C<sub>30</sub> aliphatic hydrocarbyl group, such as -(CH<sub>2</sub>)<sub>8</sub>CH=CH(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub> or -(CH<sub>2</sub>)<sub>21</sub>CH<sub>3</sub>.

14. A lubricating composition according to any of the preceding claims, wherein the composition comprises an ashless TBN booster selected from an amine-containing diblock copolymer according to Formula III:



wherein  $R^1$ ,  $R^3$ ,  $R^{2a}$ ,  $R^{2b}$ ,  $A^1$ , M, E, X, Y, Z, n, t, p and q are as defined in Claim 1; and preferably wherein  $R^3$  is a  $C_1$ - $C_{18}$  straight chain or branched alkyl group, preferably a  $C_1$ - $C_{14}$  straight chain alkyl group, such as a  $C_{12}$  straight chain alkyl group.

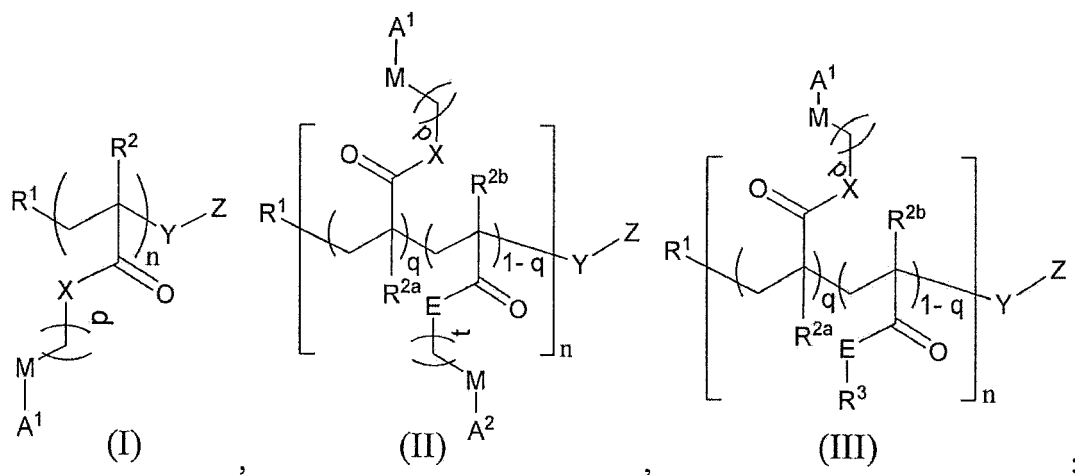
15. A lubricating composition according to any of the preceding claims, wherein n is an integer from 5 to 100, for example an integer from 5 to 50 or 5 to 25.
16. A lubricating composition according to any of the preceding claims, wherein p and/or t is an integer from 1 to 3, for example 1.
17. A lubricating composition according to any of the preceding claims, wherein the molecular weight of the block-copolymer is from 0.5 to 120 kDa, such as from 20 to 90 kDa.
18. A lubricating composition according to any of the preceding claims, wherein the TBN of the composition is at least 5 mg KOH/g, for example from 30 mg KOH/g to 50 mg KOH/g, as measured in accordance with ASTM D2896; and/or wherein the TBN of the TBN booster is at least 50 mg KOH/g, preferably at least 100 mg KOH/g, more preferably at least 150 mg/kg, as measured in accordance with ASTM D2896.
19. A lubricating composition according to any of the preceding claims, wherein the total concentration of diblock copolymer according to Formula I, II and/or III in the lubricating compositions is 0.2 % by weight or above; and/or wherein the upper limit of diblock copolymer of total concentration of diblock copolymer according to Formula I, II and/or III is 7 % by weight.
20. A lubricating composition according to any of the preceding claims, wherein the diblock copolymer of Formula I, II and/or III has a  $pK_a$  of at least 9, for example at least 10.0, as measured using a potentiometric titration with glacial acetic acid using an acetonitrile solvent.
21. A lubricating composition according to any of the preceding claims, wherein the amine-containing diblock copolymer of Formula I, II and/or III has a nitrogen content of from 1 to 10 mol.%; for example wherein the diblock copolymer is of Formula I or

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II and has a nitrogen content of from 6 to 9 mol.% or wherein the diblock copolymer is of Formula III and has a nitrogen content of from 2 to 7 mol.%.

22. A lubricating composition according to any of the preceding claims, wherein the  
 5 lubricant additive is selected from detergents, friction modifiers, dispersants, viscosity modifiers, dispersant viscosity modifiers, viscosity index improvers, pour point depressants, anti-wear additives, rust inhibitors, corrosion inhibitors, antioxidants, anti-foams, seal swell agents, extreme pressure additives, surfactants, demulsifiers, anti-seizure agents, wax modifiers, lubricity agents, anti-staining agents, chromophoric  
 10 agents, metal deactivators, and mixtures of two or more thereof.
23. A method for lubricating an internal combustion engine, for example two-stroke or four-stroke diesel engines, comprising supplying to said engine a lubricant composition as defined in any Claims 1 to 22.
- 15 24. An amine-containing diblock copolymer according to Formula I, II and/or III below:



20 wherein  $R^1$  to  $R^3$ ,  $A^1$ ,  $A^2$ ,  $M$ ,  $E$ ,  $X$ ,  $Y$ ,  $Z$ ,  $n$ ,  $t$ ,  $p$  and  $q$  are as defined in any of Claims 1 to 17.

25. Use of an amine-containing diblock copolymer according to Formula I, II and/or III as defined in any of Claims 1 to 22 for increasing ashless TBN in a lubricating oil

composition comprising a base oil of lubricating viscosity and one or more lubricant additives.

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