

# FRICION MODIFIERS AND/OR WEAR INHIBITORS DERIVED FROM HYDROCARBYL AMINES AND CYCLIC CARBONATES

## 5 Field of the Invention

The present invention relates to carbamates having improved wear inhibition and friction modifier properties as part of a lubricating oil composition.

## 10 Background of the Invention

Antiwear additives and friction modifying additives are frequently blended with lubricants in order to prevent wear, reduce fuel consumption, and increase the operating life of machinery. Glycerol esters, such as glycerol monooleate, are well known in the art as friction modifiers and as  
15 wear inhibitors. The problem associated with these compounds is that the ester functionality is easily hydrolyzed which results in the production of free oleic acid, a corrosive agent.

In this invention, more stable carbamates have been prepared by reacting oleylamine with glycerol carbonate or ethylene carbonate.  
20 Surprisingly, we have found that the reaction product of oleylamine and glycerol carbonate has exhibited good anti-wear performance and good friction performance. Previously, only glycerol monooleate had shown acceptable anti-wear performance. We have also found that the reaction product of 2-ethylhexylamine and ethylene carbonate, or the reaction product of  
25 oleylamine and ethylene carbonate, has also exhibited good friction performance.

### Summary of the Invention

This invention is directed to a lubricating oil composition comprising a major amount of base oil of lubricating viscosity and a minor amount of an additive comprising the reaction product obtained by reacting a cyclic carbonate and a hydrocarbyl amine having the formula:



in which  $R^1$  is hydrogen, or a hydrocarbyl group containing 1 to 40 carbon atoms, and  $R^2$  is a hydrocarbyl group containing 1 to 40 carbon atoms. In a preferred embodiment, the cyclic carbonate is glycerol carbonate, the hydrocarbyl amine is oleylamine, and the reaction product is glycerol carbamate. Glycerol carbmates have improved wear inhibition and friction modifier properties as part of the lubricating oil composition. In other embodiments, the carbamate is a reaction product of a cyclic carbonate, such as ethylene carbonate, and a hydrocarbyl amine such as 2-ethylhexamine or oleylamine.

### Detailed Description of the Invention

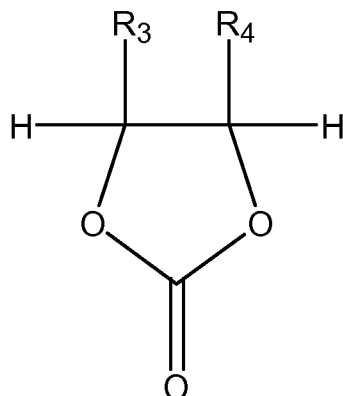
This invention relates to a carbamate additive, comprising the reaction product of a cyclic carbonate and a hydrocarbyl amine, which may be incorporated into a lubricating oil composition. Such lubricating oil compositions having this additive are particularly beneficial for reducing wear in tractor hydraulic fluids, and may be useful in other lubricating oil applications such as engine oils and gear oils. Such lubricating oil compositions having this additive may also provide for excellent friction reduction properties in the aforesaid applications.

### Definitions

The term "hydrocarbonyl" denotes a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Such groups may include the following: (1)

- 5 Hydrocarbon groups; that is, aliphatic, (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic groups, and the like. Such groups are known to those skilled in the art, and non-limiting examples include methyl, ethyl, octyl, decyl, octadecyl, cyclohexyl, phenyl, individually  
10 or in combinations thereof, etc.; (2) Substituted hydrocarbon groups; that is, groups containing non-hydrocarbon substituents which do not alter the predominantly hydrocarbon character of the group. Those skilled in the art will be aware of suitable substituents, and non-limiting examples include halo, hydroxyl, nitro, cyano, alkoxy, acyl, etc., and optionally, (3) Hetero groups;  
15 that is, groups which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and non-limiting examples include nitrogen, oxygen and sulfur.

- 20 "Cyclic carbonates" include those having the formula (I) below. An example of a cyclic carbonate wherein  $R_3$  and  $R_4$  are hydrogen is ethylene carbonate. Propylene carbonate is an example of a cyclic carbonate wherein  $R_3$  is hydrogen and  $R_4$  is a methyl group. Glycerol carbonate is an example of a cyclic carbonate wherein  $R_3$  is hydrogen and  $R_4$  is a  $CH_2-OH$  group.

Formula (I)

Carbamates are prepared by reaction of a hydrocarbyl amine and a cyclic carbonate. The hydrocarbyl amine is shown by the following formula

5 (II):

Formula (II)

10 in which  $R^1$  is hydrogen, or a hydrocarbyl group containing 1 to 40 carbon atoms, and more preferably, 8 to 28 carbon atoms and  $R^2$  is a hydrocarbyl group containing 1 to 40 carbon atoms, and more preferably 8 to 28 carbon atoms. The hydrocarbyl group in  $R^1$  and  $R^2$  may be a linear and/or branched, alkyl and/or alkenyl group. In a preferred embodiment, the cyclic carbonate is  
 15 glycerol carbonate, the hydrocarbyl amine is oleylamine, and the carbamate is glycerol carbamate.

Glycerol carbamates which are obtained by reaction of glycerol carbonate with a primary, and optionally a secondary, hydrocarbyl amine, such as saturated or unsaturated mono-amines, or mixtures of hydrocarbyl  
 20 amines derived from fatty acids, such as coco, oleyl, or tallow, preferably,

oleylamine. Non limiting examples of primary and secondary hydrocarbyl amines include octylamine, decylamine, dodecyl-amine, tetradecylamine, hexadecylamine, octadecylamine, benzylamine, phenylamine, oleylamine (for example Armeen<sup>®</sup> OLD from Akzo Nobel), stearylamine (for example Armeen  
5 18 D from Akzo Nobel), cocoamine, 2-ethylhexylamine, isotridecylamine, 2-butyl-octylamine, 2-hexyldecylamine, 2-octyldodecylamine, cyclohexylamine, , dibenzylamine, diphenylamine, dicocoamine (for example Armeen 2C from Akzo Nobel), di-2-ethylhexylamine, and N-methylcyclohexylamine,.

In another embodiment, carbamates are obtained by reaction of  
10 ethylene carbonate with a primary hydrocarbyl amine, preferably 2-ethylhexylamine. In another embodiment, carbamates are obtained by reaction of ethylene carbonate with a primary hydrocarbyl amine, preferably oleylamine.

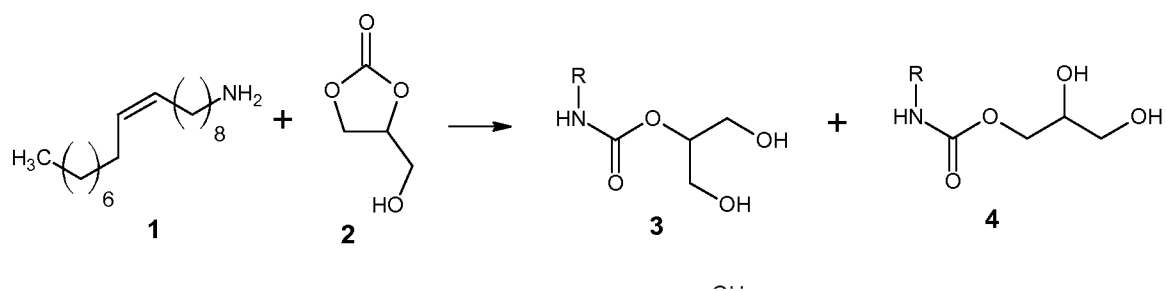
Glycerol carbonate can be produced by methods known from the prior  
15 art as described, for example, in U.S. Pat. No. 6,025,504, incorporated herein by reference in its entirety. Ethylene carbonate can be produced by methods known from the prior art as described, for example, in U.S. Pat. No. 4,314,945 and U.S. Pat. No. 4,233,221, incorporated herein by reference in its entirety.

In a preferred embodiment, glycerol carbamates are prepared by  
20 reaction of oleylamine **1** and glycerol carbonate **2**, in reaction scheme (I) below. The reaction occurs at a molar ratio of oleylamine to glycerol carbonate of 0.5:1 to 2:1, preferably 0.75:1 to 1.5:1 and more particularly 1:1, and at a temperature range of between 60 °C and 180 °C, and more preferably between 80 °C and 120 °C. A mixture of products is obtained. The

major products are glycerol carbamates, some general structures of which are shown as **3** and **4**. Minor products may include glycerol, hydroxyethylamines, and diolel urea. Hydrocarbon solvents or other inert solvents may be used in the reaction, such as benzene, toluene, and xylenes.

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Reaction scheme (I)



After the carbamate compounds of this invention are formed, they may be incorporated into a lubricating oil composition comprising a base oil of lubricating viscosity and other additive components, by the direct blending of the carbamate compounds with the lubricating oil composition. The amount of carbamate additive compounds in the lubricating oil composition is present in a "minor amount," which refers to a concentration of the additive within the lubricating oil composition of less than about 40 wt %. In some embodiments, a "minor amount" of additive refers to a concentration of the additive within the lubricating oil composition of less than about 30 wt%, of less than about 20 wt %, of less than about 10 wt %, of less than about 1 wt %, or of less than about 0.5 wt %.

### Base Oil of Lubricating Viscosity

The base oil of lubricating viscosity employed in the present invention may be mineral oils or synthetic oils. A base oil having a viscosity of at least 10 cSt ( $\text{mm}^2/\text{s}$ ) at 40° C and a pour point below 20° C, preferably at or below 5 0° C is desirable. The base oils may be derived from synthetic or natural sources. Mineral oils for use as the base oil in this invention include, for example, paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include, for example, both hydrocarbon synthetic oils and synthetic esters and mixtures thereof having 10 the desired viscosity. Hydrocarbon synthetic oils may include, for example, oils prepared from the polymerization of ethylene or higher alpha olefins (polyalphaolefin or PAO), or from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases such as in a Fisher-Tropsch process. Useful synthetic hydrocarbon oils include liquid polymers of alpha olefins 15 having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of  $\text{C}_6$  to  $\text{C}_{12}$  alpha olefins such as 1-decene trimer. Likewise, alkyl benzenes of proper viscosity, such as didodecyl benzene, can be used. Useful synthetic esters include the esters of monocarboxylic acids and polycarboxylic acids, as well as mono-hydroxy alkanols and polyols. Typical 20 examples are didodecyl adipate, pentaerythritol tetracaproate, di-2-ethylhexyl adipate, dilaurylsebacate, and the like. Complex esters prepared from mixtures of mono and dicarboxylic acids and mono and dihydroxy alkanols can also be used. Blends of mineral oils with synthetic oils are also useful. For example, blends of 10 wt % to 25 wt % hydrogenated 1-decene trimer with 75

wt % to 90 wt % 150 SUS (100F.) mineral oil make excellent lubricating oil bases.

#### Other Additive Components

The following additive components are examples of some other  
5 additive components that can be favorably employed in the present invention. These examples of additives are provided to illustrate the present invention, but they are not intended to limit it:

(1) Ashless dispersants: alkenyl succinimides, alkenyl succinimides modified with other organic compounds, and alkenyl succinimides modified with boric  
10 acid, alkenyl succinic ester.

(2) Oxidation inhibitors: (a) Phenol type oxidation inhibitors: 4,4'-methylene bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene bis(4-methyl-6-tert-butyl-phenol), 4,4'-butylidenebis(3-methyl-6-tert-butylphenol), 4,4'-isopropyl-idenebis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6dimethyl-phenol), 2,2'-methylenebis (4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methyl-phenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol, 2,6-di-tert-4-(N,N'-dimethyl-aminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol),  
15 bis(3-methyl-4-hydroxy-5-tert-butyl benzyl)sulfide, and bis (3,5-di-tert-butyl-4-hydroxybenzyl). (b) Diphenylamine type oxidation inhibitor: alkylated diphenylamine, phenyl-.alpha.-naphthylamine, and alkylated alpha-naphthylamine (c) Other types: metal dithiocarbamate (e.g., zinc  
20

dithiocarbamate), molybdenum oxysulfide succinimide complexes, and methylenebis (dibutyl-dithiocarbamate).

(3) Rust inhibitors (Anti-rust agents) (a) Nonionic polyoxyethylene surface active agents: polyoxyethylene lauryl ether, polyoxyethylene higher alcohol

5 ether, polyoxyethylene nonylphenyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol monooleate. (b) Other compounds: stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal  
10 salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.

(4) Demulsifiers: addition product of alkylphenol and ethyleneoxide, polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester.

(5) Extreme pressure agents (EP agents): zinc dialkyldithiophosphate (aryl  
15 zinc, primary alkyl, and secondary alkyl type), sulfurized oils, diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene, fluoroalkylpolysiloxane, and lead naphthenate.

(6) Multifunctional additives: sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphoro dithioate, oxymolybdenum  
20 monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complex compound, and sulfur-containing molybdenum complex compound.

(7) Viscosity index improvers: polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-

isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

(8) Pour point depressants: polymethyl methacrylate.

(9) Foam Inhibitors: alkyl methacrylate polymers and dimethyl silicone

5 polymers. (11) Metal detergents: sulfurized or unsulfurized alkyl or alkenyl

phenates, alkyl or alkenyl aromatic sulfonates, sulfurized or unsulfurized metal

salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl

hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl

naphthenates, metal salts of alkanoic acids, metal salts of an alkyl or alkenyl

10 multiacid, and chemical and physical mixtures thereof. Non-limiting examples

of suitable metals include alkali metals, alkaline metals and transition metals.

In some embodiments, the metal is Ca, Mg, Ba, Sr, K, Na, Li or the like.

The base oil of the present invention is present in a "major amount." A

"major amount" of a base oil of lubricating viscosity refers to a concentration

15 of the oil within the lubricating oil composition of at least about 40 wt %. In

some embodiments, "a major amount" of a base oil of lubricating viscosity

refers to a concentration of the oil within the lubricating oil composition of at

least about 50 wt %, at least about 60 wt %, at least about 70 wt %, at least

about 80 wt %, or at least about 90 wt %.

20 To further illustrate the additive and the lubricating oil compositions of

this invention, the following non-limiting examples are provided.

### Examples

#### EXAMPLE 1

##### 5                   Reaction Product of Oleylamine and Glycerol Carbonate

A 1 L glass reactor equipped with an agitator was charged with oleylamine (473.96 g, 1.80 mole based on an amine value of 213 mg KOH/g; available from Akzo Nobel as Armeen<sup>®</sup> OLD) under a nitrogen atmosphere and heated  
10 to 100°C. Glycerol carbonate (212.47 g, 1.80 mole; available from Huntsman as JEFFSOL<sup>®</sup> glycerol carbonate) was added via an addition funnel over 2 hours. The reaction mixture was heated at 100°C for an additional 5 h.

#### EXAMPLE 2

15

##### Reaction Product of Oleylamine and Glycerol Carbonate

A 500 mL glass reactor equipped with an agitator was charged with oleylamine (221.63 g, 0.84 mol based on an amine value of 213 mg KOH/g)  
20 under a nitrogen atmosphere and heated to 100°C. Glycerol carbonate (99.35 g, 0.84 mol) was added via an addition funnel over several minutes. The reaction mixture was heated at 100°C for an additional 4 h.

#### EXAMPLE 3

25

##### Reaction Product of Oleylamine and Glycerol Carbonate

A 500 mL glass reactor equipped with an agitator was charged with oleylamine (217.53 g, 0.826 mole based on amine value of 213 mg KOH/g)  
30 under a nitrogen atmosphere and heated to 155°C. Glycerol carbonate (97.52 g, 0.826 mol) was added via a syringe pump over 2 hours. The reaction mixture was heated at 160°C for an additional 4 h.

## EXAMPLE 4

## Reaction Product of Dodecylamine and Glycerol Carbonate

5 A 500 mL glass reactor equipped with an agitator was charged with dodecylamine (281.35 g, 1.52 mol) under a nitrogen atmosphere and heated to about 70°C. Glycerol carbonate (179.24 g, 1.52 mol) was added via an addition funnel over several minutes. The reaction mixture was heated at 70°C for an additional 2.5 h.

10

## EXAMPLE 5

## Reaction Product of Oleylamine and Glycerol Carbonate

15 A 1 L glass reactor equipped with an agitator was charged with oleylamine (462.61 g, 1.76 mol) under a nitrogen atmosphere and heated to about 160°C. Glycerol carbonate (207.38 g, 1.76 mol) was added via an addition funnel over several minutes. The reaction mixture was heated at 160°C for an additional 4.5 h.

20

## EXAMPLE 6

## Reaction Product of Oleylamine and Glycerol Carbonate

25 A 500 mL glass reactor equipped with an agitator was charged with oleylamine (256.15 g, 0.97 mol based on amine value of 213 mg KOH/g) under a nitrogen atmosphere and heated to about 70°C. The reactor was placed in a cooling water bath to remove the heat of reaction and keep the reaction mixture temperature below 90°C. Glycerol carbonate (114.83 g, 0.97  
30 mol) was added via an addition funnel over several minutes. The reaction mixture was heated at 70°C for approximately an additional 3 h.

## EXAMPLE 7

## 5                   Reaction Product of Oleylamine and Ethylene Carbonate

A 500 mL glass reactor equipped with an agitator was charged with oleylamine (327.20 g, 1.24 mol based on amine value of 213 mg KOH/g) under a nitrogen atmosphere and heated to about 70°C. The reactor was  
10 placed in a cooling water bath to remove the heat of reaction and keep the reaction mixture temperature at about 70°C. Ethylene carbonate (109.38 g, 1.24 mol) was added via a syringe pump over several minutes. The reaction mixture was heated at 70°C for approximately an additional 4 h.

## 15                   EXAMPLE 8

## Reaction Product of 2-Ethylhexylamine and Ethylene Carbonate

A 500 mL glass reactor equipped with an agitator was charged with  
20 oleylamine (164.06 g, 1.27 mol) under a nitrogen atmosphere and heated to about 70°C. The reactor was placed in a cooling water bath to remove the heat of reaction and keep the reaction mixture temperature at about 70°C. Ethylene carbonate (111.8 g, 1.27 mol) was added via a syringe pump over several minutes. The reaction mixture was heated at 70°C for approximately  
25 an additional 4 h.

30

## PERFORMANCE EXAMPLES

## Anti-Wear Properties

5           The anti-wear properties of the following examples were evaluated in a formulated baseline oil. This formulated oil comprised a lubricating oil and additives in their typical amounts for particular purpose; this included a zinc dialkyldithiophosphate, a mixture of calcium-containing detergents, a seal swell additive and a corrosion inhibitor.

10           The formulated baseline oil was then top-treated with either 0.3 wt. % of the glycerol carbamate of Example 2 or 0.3 wt % of glycerol monooleate, a standard anti-wear additive. The three formulations were then evaluated in the proprietary ZF-Standard V3, S19-2 Wear Test Method available from ZF Friedrichshafen. The results are summarized in Table 1.

15

TABLE 1  
ZF Standard Gear Wear Test Results

| Formulation                    | Weight Loss (mg) |
|--------------------------------|------------------|
| Baseline                       | 577              |
| Baseline + glycerol monooleate | 8                |
| Baseline + Example 2           | 13               |

20           The lubricating oil composition containing glycerol carbamate of Example 2 demonstrated comparable anti-wear properties to the lubricating oil composition containing glycerol monooleate.

## Friction Modifier Properties

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The frictional properties of the following examples were evaluated in a formulated baseline oil. This formulated oil comprised a 45N Group II lubricating oil and additives in their typical amounts for particular purpose; this

included 4.0 wt. % succinimide 48.5 millimoles of a mixture of calcium containing detergents, 7 millimoles of a mixture of primary and secondary zinc dithiophosphates, 1.2 wt. % of an antioxidant, 0.5 wt. % of a suflurized/molybdated succinimide complex , 0.3 wt. % of a pour point  
5 depressant , 10 ppm of a foam inhibitor and 4.8 wt. % of a viscosity index improver.

The formulated baseline oil was then top-treated with either 0.5 wt. % of Example 2 or 0.5 wt % of a borated glycerol monooleate, a conventional friction modifier. The three formulations were then evaluated in a proprietary  
10 mini traction machine (MTM) friction test available from PCS Instruments. This MTM friction test applies a certain load between a steel ball and disk. The ball is rolling as well as sliding relative the disk. The load, speed is designed into a profile that covers all the friction conditions of a gasoline engine. While testing, the ball and the disk are immersed in the lubricating oil  
15 to evaluate the lubricating effect of this oil (meaning that the friction coefficient between the ball and disk is measured under this profile with the lubricating oil). The results are summarized in Table 2.

TABLE 2  
MTM Friction Test Results

| Formulation                            | Integration of Total Friction |
|----------------------------------------|-------------------------------|
| Baseline                               | 139.67                        |
| Baseline + borated glycerol monooleate | 101.24                        |
| Baseline + Example 2                   | 83.27                         |
| Baseline + Example 8                   | 83.36                         |
| Baseline + Example 7                   | 109.62                        |

5

The lubricating oil composition containing glycerol carbamate demonstrated superior anti-friction properties to the lubricating oil composition containing glycerol monooleate.

That which is claimed:

1. A lubricating oil composition comprising a major amount of base oil of lubricating viscosity and a minor amount of an additive comprising the reaction product obtained by reacting a cyclic carbonate and a hydrocarbyl amine having the formula (I):



- in which  $R^1$  is hydrogen, or a hydrocarbyl group containing 1 to 40 carbon atoms, and  $R^2$  is a hydrocarbyl group containing 1 to 40 carbon atoms.

2. The lubricating oil composition of claim 1 wherein  $R^1$  is hydrogen, or a hydrocarbyl group containing 8 to 28 carbon atoms.

3. The lubricating oil composition of claim 2, wherein said hydrocarbyl comprises a linear and/or branched, alkyl and/or alkenyl group.

4. The lubricating oil composition of claim 1 wherein  $R^2$  is a hydrocarbyl group containing 8 to 28 carbon atoms.

5. The lubricating oil composition of claim 4, wherein said hydrocarbyl comprises a linear and/or branched, alkyl and/or alkenyl group.

6. The lubricating oil composition of claim 1 wherein said hydrocarbyl amine is a primary amine.

7. The lubricating oil composition of claim 1 wherein said cyclic carbonate is selected from the group consisting of ethylene carbonate, propylene carbonate, and glycerol carbonate.

8. The lubricating oil composition of claim 1 further comprising at least one co-additive selected from: (a) an ashless dispersant; (b) an oxidation inhibitor; (d) a demulsifier; (e) an extreme pressure agent; (f) a multifunctional additive; (g) a viscosity index improver; (h) a pour point depressant; (i) a foam inhibitor; and (j) an emulsifier.

9. The lubricating oil composition of claim 1 wherein said reaction of said cyclic carbonate and said hydrocarbyl amine occurs at a molar ratio of hydrocarbyl amine to cyclic carbonate of 0.5:1 to 2:1 and at a temperature range of between 60 °C and 180 °C.

10. The lubricating oil composition of claim 9 wherein said hydrocarbyl amine comprises oleylamine, and wherein said cyclic carbonate comprises glycerol carbonate.

11. The lubricating oil composition of claim 1 wherein said hydrocarbyl amine comprises 2-ethylhexylamine, and wherein said cyclic carbonate comprises ethylene carbonate.

12. The lubricating oil composition of claim 1 wherein said hydrocarbyl amine comprises oleylamine, and wherein said cyclic carbonate comprises glycerol carbonate.

13. The lubricating oil composition of claim 1 wherein said reaction product is formed prior to addition to said base oil of lubricating viscosity.

14. The process of claim 1 wherein said additive is a wear inhibitor or a friction modifier.