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3,706,667

MONOSUBSTITUTED UREAS IN LUBRICATING COMPOSITIONS

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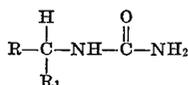
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U.S. Cl. 252-51.5 A

10 Claims

ABSTRACT OF THE DISCLOSURE

Varnish-removing additives for lubricating compositions comprising monosubstituted ureas having the formula



wherein R is hydrogen, alkyl or alkenyl and R₁ is alkyl or alkenyl, and the sum of the carbon atoms in R and R₁ is from about 5 to about 25.

The present invention relates to lubricating compositions. More specifically, it relates to lubricating compositions having improved varnish-removing characteristics.

Lubricating compositions are susceptible to oxidation and deterioration in applications such as internal combustion engines. The oxidation and deterioration are characterized by the formation of organic acids, aldehydes, ketones, etc., resulting in the formation of products which have a tendency to agglomerate to form sludge and varnish-like deposits.

Present day internal combustion engines operate at high speeds and high compression ratios. When used in the so-called city stop-and-go driving, which includes the greater part of the driving conditions for a large percentage of today's automobiles, the internal combustion engines do not reach the most efficient operating temperatures. Under city driving conditions, large amounts of partial oxidation products are formed, and reach the crankcase of the engine by blowing past the piston rings. Most of these partial oxidation products are oil insoluble, tending to form deposits on the various operating parts of the engine such as the pistons, piston rings, etc. For the purpose of preventing the deposition of these products on the various engine parts, it is advantageous to incorporate detergents in the lubricating compositions, thus keeping these polymeric oxidation products highly dispersed in a condition unfavorable for deposit on metals.

While oxidation inhibiting additives and detergent additives have proven advantageous in reducing the formation of varnish on engine parts, varnish deposits are still commonly encountered after prolonged engine operation. The deposit of varnish and sludge on the interior surface of automotive, aviation and diesel engines and the accumulation of these deposits in the oil used to lubricate such engines deleteriously affects their operation and in many instances gives rise to engine failure.

The prior art discloses certain lubricating additives designed to retard the formation of varnish deposits. In contrast therewith, the present invention discloses a particular class of lubricant additives which is effective in removing varnish deposits after they have formed on engine parts, thus behaving as a varnish stripper.

It is an object of the present invention, therefore, to provide improved lubricating compositions having varnish-removing characteristics. Another object of the present invention is to provide additives for lubricants which act

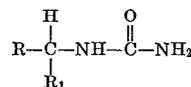
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as varnish strippers. Other aspects, objects and advantages of the present invention will be apparent from a consideration of the accompanying disclosure and the appended claims.

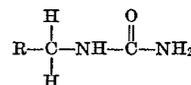
In the present invention it was discovered that certain monosubstituted ureas, when employed in small amounts in a lubricating composition, are effective in removing varnish and other deposits from parts exposed to the lubricant, for example, the cylinder walls, piston rings and valve mechanisms of internal combustion engines. It was found in the present invention that, within the class of substituted ureas, only monosubstituted ureas are outstanding in removing deposits from engine parts when employed in the lubricant. Disubstituted urea compounds, for example, do not provide the outstanding results achieved by the use of monosubstituted ureas.

It was further discovered in the present invention that, even among the monosubstituted urea compounds, only certain of those compounds exhibit outstanding activity in removing varnish of the type found on internal combustion engine parts exposed to the lubricant. More particularly, successful results were achieved in the present invention with monosubstituted ureas wherein the substitution group has a total carbon number of from about 5 to about 25.

The monosubstituted urea compounds which are employed as lubricant additives in the present invention are represented by the following structures:



where R₁ is hydrogen, alkyl or alkenyl and R is alkyl or alkenyl, and the sum of the carbon atoms in R and R₁ is from about 5 to about 25 and



where R is alkyl or alkenyl having from 5 to 25 carbon atoms.

Preferred compounds are those monosubstituted ureas where the substituent group is primary alkyl or primary alkenyl having at least about 9 carbon atoms. Outstanding results have been achieved with octadecylurea, dodecylurea and 9-octadecenyl urea.

The outstanding activity of the monosubstituted ureas of the present invention as varnish removers is illustrated by the results of a bench test wherein numerous urea compounds were brought into contact with a test strip coated with resinous deposits of the kind typically found in automotive engines. The resinous deposits used for the bench test were obtained from a Sequence VB test engine which had operated on a mineral lubricating oil. This type test is one of the group known as the Engine Test Sequences for Evaluating Oils for API Service MS (1963). Sequence V is designed to measure the ability of a lubricant to prevent or reduce engine deposits products by low- and medium temperature operating conditions. In this sequence, which places emphasis on the antisludging, anticlogging and insolubles suspension characteristics of a lubricant, a 1957 Lincoln-Mercury engine is used and thus the test is often referred to as the Lincoln Engine Test. The engine conditions of the Lincoln Engine Test are typical of the conditions encountered in present-day "stop-and-go" driving.

With further reference to the bench test, some of the urea compounds tested were not soluble in engine oil at room temperature. Accordingly, all of the compounds

were dissolved in a hot mineral lubricating oil (0.1 g. of urea compound in 20 g. SAE 10W-30 base oil at 105° C.). A stainless steel spatula was coated in the following manner with resinous deposits from the Sequence VB engine test run. The spatula was dipped into dimethylformamide solvent containing approximately 20% by weight of the resinous deposits, and the coating was then allowed to dry. The coated spatula was then immersed in the hot oil-urea solution for 30 minutes, removed, allowed to cool and wiped with a tissue. The portion of resin removed after wiping was visually estimated and defined as the activity percentage. Results obtained with various substituted urea compounds are set forth in Table I below wherein the substituent groups correspond to the following structure:

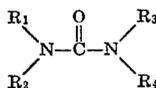


TABLE I.—VARNISH REMOVAL ACTIVITY OF SUBSTITUTED UREAS
[0.5% in oil at 105° C.]

Compound	R ₁	R ₂	R ₃	R ₄	Activity percent
1-cyclohexyl-3-octadecylurea	C ₈ H ₁₇ —	H	H	C ₁₈ H ₃₇ —	0
Tetrabutylurea	C ₄ H ₉ —	C ₄ H ₉ —	C ₄ H ₉ —	C ₄ H ₉ —	0
Octadecylurea	C ₁₈ H ₃₇ —	H	H	H	99
t-Butylurea	—C(CH ₃) ₃	H	H	H	0
1,3-dimethylurea	—CH ₃	H	H	H	10
1,3-diethylurea	—C ₂ H ₅	H	H	H	10
Butylurea	—C ₄ H ₉	H	H	H	10
1,1-dibutylurea	—C ₄ H ₉	—C ₄ H ₉	H	H	0
Allylurea	—C ₃ H ₅	H	H	H	0
t-Amylurea	—t-C ₅ H ₁₁	H	H	H	0
Methylurea	—CH ₃	H	H	H	10
1,3-diisopropylurea	(CH ₃) ₂ CH—	H	(CH ₃) ₂ CH—	H	0
1-cyclohexyl-1,3-pentylurea	C ₆ H ₁₁ —	H	C ₅ H ₁₁ —	H	0
Dodecylurea	—n-C ₁₂ H ₂₅	H	H	H	99
1-cyclohexyl-3,3-diethylurea	—C ₆ H ₁₁	—C ₂ H ₅	—C ₂ H ₅	—C ₂ H ₅	0
1-cyclohexyl-3,3-diethyl-1-methylurea	—C ₆ H ₁₁	—C ₂ H ₅	—C ₂ H ₅	—C ₂ H ₅	0
1-cyclohexyl-1,3,3-triethylurea	—C ₆ H ₁₁	—C ₂ H ₅	—C ₂ H ₅	—C ₂ H ₅	0
1-sec-butyl-1-cyclohexyl-3,3-diethylurea	—C ₆ H ₁₁	—sec-C ₄ H ₉	—C ₂ H ₅	—C ₂ H ₅	0
1-cyclohexyl-1,3,3-trimethylurea	—C ₆ H ₁₁	—CH ₃	—CH ₃	—CH ₃	0
1-cyclohexyl-1-ethyl-3,3-dimethylurea	—C ₆ H ₁₁	—C ₂ H ₅	—CH ₃	—CH ₃	0
1-cyclohexyl-3,3-dimethylurea	—C ₆ H ₁₁	H	—CH ₃	—CH ₃	15
1-cyclohexyl-3-methylurea	—C ₆ H ₁₁	H	—CH ₃	H	5
1-cyclohexyl-1,3-dimethylurea	—C ₆ H ₁₁	—CH ₃	—CH ₃	H	5
1,1-dimethyl-3-(2-ethylcyclohexyl) urea	—CH ₃	—CH ₃	—(2-EtC ₆ H ₁₀)	—H	0
1-cyclohexyl-1-ethyl-3-methylurea	—C ₆ H ₁₁	—C ₂ H ₅	—CH ₃	—H	0
1-tert-butyl-3-methyl-1-(5,5,7,7)tetramethyl-2-octenylurea	—t-C ₄ H ₉	—t-C ₈ H ₁₇	—CH ₃	—C ₈ H ₁₅	0
1-butyl-1-cyclohexyl-3-methylurea	—C ₆ H ₁₁	—C ₄ H ₉	—CH ₃	H	0
1-cyclohexyl-3-methyl-1-propylurea	—C ₆ H ₁₁	—C ₃ H ₇	—CH ₃	H	5
1-butyl-tert-butyl-3-methylurea	—C ₄ H ₉	—t-C ₄ H ₉	—CH ₃	H	0
1-tert-butyl-1-isobutyl-3-methylurea	—t-C ₄ H ₉	—t-C ₄ H ₉	—CH ₃	H	0
N,N-dimethylurea-N',N'-diheptylurea	—CH ₃	—CH ₃	—C ₇ H ₁₅	—C ₇ H ₁₅	20
N,N-diethyl-N',N'-diheptylurea	—C ₂ H ₅	—C ₂ H ₅	—C ₇ H ₁₅	—C ₇ H ₁₅	0
1,1,3,3-tetramethylurea	—CH ₃	—CH ₃	—CH ₃	—CH ₃	0
1-(2,6-diethylcyclohexyl)3,3-dimethylurea	—(2,6-di-Et-C ₆ H ₉)	H	—CH ₃	—CH ₃	0
1-(2-tert-butyl-5,6-dimethylcyclohexyl)3,3-dimethylurea	—(1-t-Bu-5,6-di-Me-C ₆ H ₉)	H	—CH ₃	—CH ₃	10
1-(2-tert-butyl-6-ethylcyclohexyl)3,3-dimethylurea	—(2-t-Bu-6-Et-C ₆ H ₉)	H	—CH ₃	—CH ₃	0
1-tert-butyl-3-(2-tert-butyl-6-methylcyclohexyl)urea	—(2-t-Bu-6-Me-C ₆ H ₉)	H	—t-C ₄ H ₉	H	5
1,1-diethyl-3-methylurea	—C ₂ H ₅	—C ₂ H ₅	—CH ₃	H	0
t-Dodecylurea	t-C ₁₂ H ₂₅	H	H	H	50
9-octadecenylurea	—C ₁₈ H ₃₅	H	H	H	99
1,1,3-trimethylurea	—CH ₃	—CH ₃	—CH ₃	H	0
2-ethylhexylurea	—2Et-C ₆ H ₁₂	H	H	H	0

¹ Film became soft and mottled.

From the data in Table I it can be seen that the greatest varnish removal activity was achieved with the following primary monosubstituted ureas: octadecylurea, dodecylurea, dodecylure and 9-octadecenylurea. The advantage of primary substitution is illustrated by the 99% activity of dodecylurea as compared to 50% activity of tertiary dodecylurea.

To demonstrate the effectiveness of monosubstituted ureas as varnish removers for engine parts, an engine test was conducted using 9-octadecenylurea according to the following example:

EXAMPLE 1

9-Octadecenylurea was added to a quantity of SAE 10W-30 base oil at a concentration of 2 percent by weight. A zinc phosphorodithioate inhibitor was added to the oil at a concentration of 1.4 percent by weight. The crankcase of a Sequence VB test engine having varnish and sludge on the engine parts was filled with the urea-containing oil. After 2 hours of operation, the engine was disassembled and inspection revealed that partial cleaning of the engine parts had taken place. Higher concen-

trations than 2 percent of the urea additive in the oil are preferable for more effective cleaning.

Monosubstituted ureas useful in the lubricating compositions of the present invention may be prepared according to numerous known processes. Processes for the manufacture of monoalkylsubstituted ureas have involved the reaction of alkyl isocyanates with ammonia, the reaction of ammonium salts with alkali metal cyanates and the reaction of nitrourea with amines. Still another process comprises reacting an alkyl amine with urea in approximately equivalent molecular proportions and then heating the mixture to a temperature between 100° C. and the decomposition temperature of the desired alkyl urea. Yet another process comprises the reaction of carbon monoxide, sulfur and an amine.

Typical examples of the substituents which may be present in the monosubstituted ureas of the present invention are alkyl radicals, e.g., amyl, hexyl, heptyl, octyl,

nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl and other branched alkyl radicals having the formula C_nH_{2n+1} where n is an integer up to 25; alkenyl radicals, e.g., pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, dodecenyl and other alkenyl radicals having the formula C_nH_{2n-1} where n is an integer up to 25.

The base stock into which the monosubstituted ureas of the present invention are incorporated can be of lubricating viscosity and can be a mineral oil or a synthetic lubricant. The mineral lubricating oils can be, for instance, solvent extracted or solvent refined oils obtained in accordance with conventional methods of solvent refining lubricating oils. Frequently, the viscosity of these mineral oils will be about 20 to 250 SUS at 210° F. The mineral base oil may, for example, be derived from paraffinic, naphthenic, asphaltic or mixed base petroleum crudes, and if desired, a blend of solvent-treated Mid-Continent neutrals and Mid-Continent bright stocks may be employed.

Synthetic lubricants to which the monosubstituted ureas of the present invention may be added include ester-base synthetic lubricants of lubricating viscosity which consist

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essentially of carbon, hydrogen and oxygen, e.g., di-2-ethylhexyl sebacate. Various of these lubricating materials have been described in the literature and generally their viscosity ranges from light to heavy, e.g., about 50 SUS at 100° F. to 250 SUS at 210° F., preferably 30 to 150 SUS at 210° F. The complex esters, diesters, monoesters and polyesters may be used alone or, to achieve the most desirable viscosity characteristics, complex esters, diesters and polyesters may be blended with each other or with naturally occurring esters like castor oil to produce lubricating compositions of wide viscosity ranges.

Various useful ester base stocks are disclosed in U.S. Pats. Nos. 2,499,983; 2,499,984; 2,575,195; 2,575,196; 2,703,811; 2,705,724; and 2,723,286. Generally, the synthetic base stocks consist essentially of carbon, hydrogen and oxygen, i.e., the essential nuclear chemical structure is formed by these elements alone. However, these structures may be substituted with other elements such as halogens, e.g., chlorine and fluorine. Some representative components of ester lubricants are ethyl palmitate, ethyl stearate, di-(2-ethylhexyl) sebacate, ethylene glycol dilaurate, di-(2-ethylhexyl) phthalate, di-(1,3-methylbutyl) adipate, di-(2-ethylbutyl) adipate, di-(1-ethylpropyl) adipate, diethyl oxylate, glycerol tri-n-acetate, dicyclohexyl adipate, di(undecyl) sebacate, tetraethylene glycol di-(2-ethylene hexoate), di-Cellosolve phthalate, butyl phthallyl butyl glycolate, di-n-hexyl fumarate polymer, dibenzyl sebacate and diethylene glycol bis-(2-n-butoxy ethyl carbonate); 2-ethyl-hexyl-adipate-neopentyl glycol-adipate-2-ethylhexyl is a representative complex ester.

Other synthetic stocks to which the monosubstituted ureas of the present invention may be added are the polyphenyl ethers, aromatic sulfides and thioethers. Useful thioether base stocks are described in U.S. Pats. Nos. 3,096,375 and 3,119,877. Polyphenyl ether base stocks are described in U.S. Pats. Nos. 3,173,873 and 3,184,430.

The compositions of the present invention incorporate a minor amount of a monosubstituted urea sufficient to provide the base stock of lubricating viscosity, which is the major component of the composition, with varnish-removing properties. This amount is generally from about 0.1 to about 10 weight percent or more depending on the particular base stock used and its application. The preferred concentration is from about 3 to about 6 percent by weight.

The lubricating compositions of the present invention will generally contain minor amounts of addition agents besides monosubstituted ureas. Thus, for example, it is particularly advantageous in many instances to add an anti-foam agent to the lubricating composition. Other addition agents can be added to the lubricant for a specific purpose such as an anti-oxidant, pour point depressant, dispersant, corrosion inhibitor, viscosity index improver, oiliness and extreme pressure agent and the like.

Those monosubstituted ureas of the present invention which are not soluble in the lubricant base stock at room temperature can be solubilized by small amounts of strong acid (0.5 mole of HCl or 1 mole of benzene sulfonic acid)

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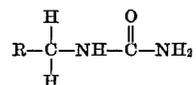
or larger amounts of weak acids (approximately 2 to 3 moles of acetic acid). The action of the acid is to eliminate the crystallinity by salt formation. It has also been found that neutral calcium alkylbenzene sulfonate will solubilize 9-octadecenyurea.

The heat generated in the crankcase or sump of an internal combustion engine promotes solubility of many monosubstituted ureas in the lubricating oils. This, in turn, enhances the varnish-removing activity.

While this invention has been described with respect to various specific examples and embodiments, it is understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. A lubricating composition comprising a major amount of a hydrocarbon base stock of lubricating viscosity and a minor amount, sufficient to impart varnish-removing activity, of a compound having the formula



where R is alkyl or alkenyl having from 5 to 25 carbon atoms.

2. A composition of claim 1 where R contains at least about 9 carbon atoms.

3. A composition of claim 1 wherein the compound is octadecenyurea.

4. A composition of claim 1 wherein the compound is dodecenyurea.

5. A composition of claim 1 wherein the compound is 9-octadecenyurea.

6. A composition of claim 1 wherein the base stock is a mineral lubricating oil.

7. A composition of claim 1 wherein the base stock is an ester-based lubricant.

8. A composition of claim 1 wherein the base stock is a polyphenyl ether lubricant.

9. A composition of claim 1 wherein the base stock is a thioether.

10. A composition of claim 1 wherein the compound is present in a concentration from about 0.1 weight percent to about 10 weight percent, based upon the hydrocarbon base stock.

References Cited

UNITED STATES PATENTS

2,195,167	3/1940	Egerton	252—51.5 A
2,698,300	12/1954	Hotten	252—51.5 A
2,993,930	7/1961	Chappelow et al.	252—51.5 A

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