United States Patent Office 3,182,024 Patented May 4, 1965

3,182,024

POLYAMINOPYRROLIDINES IN LUBRICATING OILS

Frank A. Stuart, Orinda, and Robert G. Anderson, Novato, Calif., assignors to California Research Corporation, San Francisco, Calif., a corporation of Delaware

No Drawing. Filed Mar. 19, 1963, Ser. No. 266,160
10 Claims. (Cl. 252—50)

This invention pertains to lubricating oil compositions containing metal-free detergents having acid-neutralizing characteristics.

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 temperature. 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 necessary to incorporate detergents in the lubricating oil compositions, thus keeping these polymeric products highly dispersed in a condition unfavorable for deposition on metals.

For the most part, the various detergents which are added to crankcase oils to reduce this formation of sludges and varnishes are metal organic compounds, particularly those compounds wherein the metal is linked to an organic group through an oxygen atom. Although these metal-containing organic compounds have some effectiveness as detergents for dispersing the precursors of deposits within the oil itself rather than permitting them to form added deposits on the engine parts, they have the disadvantage of forming ash deposits in the engine. These ash deposits lower engine performance by fouling spark plugs and valves, and contribute to preignition.

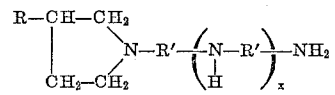
It is a particular object of this invention to provide lubricating oil compositions which are compounded with metal-free detergents having acid-neutralizing characteristics.

Therefore, in accordance with this invention, it has been discovered that lubricating oil compositions particularly useful for heavy duty service are obtained by incorporating certain N-polyaminopyrrolidines in oils of lubricating viscosity.

The polyaminopyrrolidines described herein are effective not only as detergents in lubricating oil compositions, but they also effectively neutralize acids which are formed. Thus, by the use of lubricating oil compositions containing the particular pyrrolidines described herein, diesel and gasoline engine parts remain remarkably free of deposits and varnish, even under severe operating conditions.

These polyaminopyrrolidines are 1-aminoalkyl-3-alkenylpyrrolidines wherein the alkenyl radical has at least 30 carbon atoms, more preferably 50 to 200 carbon atoms, and the alkyl radical has from 2 to 6 carbon atoms. These also include the 1-polyaminoalkyl-3-alkenyl pyrrolidines.

The polyaminopyrrolidines can be represented by the formula:



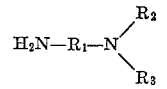
wherein R is an alkenyl radical having from 30 to about 200 carbon atoms, R' is a divalent alkylene radical having from 2 to 6 carbon atoms, and x is a number from

0 to 8. The R' radicals may be derived from polyalkylene polyamine reactants.

These pyrrolidines can be obtained by first preparing the pyrrolidinedione by the reaction of an olefinic hydrocarbon with maleic anhydride. The resulting alkenyl succinic anhydride is then reacted with the desired polyamine to form the pyrrolidinedione, which then can be reduced (hydrogenated) to form the corresponding pyrrolidine.

Examples of polyalkylene polyamine reactants include diethylene triamine, dipropylene triamine, tetraethylene pentamine, pentaethylene hexamine, nonaethylenenedecamine, dihexamethylene triamine, etc.

In addition to polyalkylene polyamine reactants, other amines can be used, such as, alkylaminoalkylene amines of the formula:



wherein R_1 is an alkylene radical, and R_2 and R_3 are alkyl radicals having from 1 to 4 carbon times. The sum of carbon atoms in R_1, R_2 and R_3 is preferably from 3 to 10.

The polyaminopyrrolidines can be prepared by reducing the corresponding alkenyl pyrrolidinedione.

Lubricating oils which can be used as base oils include a wide variety of lubricating oils, such as naphthenic base, paraffin base, and mixed base lubricating oils, other hydrocarbon lubricants, e.g., lubricating oils derived from coal products, and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc., and the mixtures thereof), alkylene oxide-type polymers (e.g., propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing the alkylene oxide in the presence of water or alcohols, e.g., ethyl alcohol, dicarboxylic acid esters (such as those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid suberic acid, sebacic acid, alkanol succinic acid, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethyl hexyl alcohol, dodecyl alcohol, etc.), liquid esters of acids of phosphorus, alkyl benzenes (e.g., monoalkyl benzene such as dodecyl benzene, tetradecyl benzene, etc., and dialkyl benzenes (e.g., n-nonyl 2-ethyl hexyl benzene); polyphenyls (e.g. biphenyls and terphenyls), alkyl biphenyl ethers, polymers of silicon (e.g., tetraethyl silicate, tetraisopropyl silicates, tetra(4-methyl-2-tetraethyl) silicate, hexyl (4-methyl-2-pentoxy) disiloxane, poly(methyl) siloxane, poly(methylphenyl) siloxane, etc.

The above base oils may be used individually or in combinations thereof, wherever miscible or wherever made so by the use of mutual solvents.

These pyrrolidines can be used in oils of lubricating viscosity in amounts of 0.1% to 30% by weight, preferably 0.25% to 5%, by weight.

The following examples illustrate the preparation of the pyrrolidines described herein.

EXAMPLE I.—PREPARATION OF 1-(TRIETHYLENETETRAMINOETHYL)-3 - POLYISOBUTENYL PYRROLIDINE

Forty-two grams of lithium aluminum hydride was dissolved in 9 liters of ethyl ether. Twelve hundred grams of approximately 45% petroleum oil solution of N-tetraethylene pentamine polyisobutenylpyrrolidine-dione, wherein the polyisobutenyl radical had a molecular weight of about 850 (the oil solution having a nitrogen content of 1.78%), was added to the ether solution over a period of 3 hours so as to maintain a gentle reflux. This solution was stirred while refluxing for an addi-

tional 6 hours. Thirty milliliters of water was slowly added over a period of 3 hours to decompose unreacted lithium aluminum hydride followed by the addition of 470 ml. of water. The mixture was allowed to settle and the ether layer was decanted and filtered. The ether solution was washed with aqueous sodium carbonate solution, centrifuged, dried over anhydrous sodium carbonate, filtered, and freed of solvent under vacuum.

The final product which had a nitrogen content of 1.50% of which 1.13% was basic nitrogen, was essentially free of lithium and aluminum. Infrared analysis showed that the carbonyl groups present in the original pyrrolidinedione were no longer present.

EXAMPLE II.—PREPARATION OF 1-(TRIETHYLENETETRAMINOETHYL)-3 - POLYISOBUTENYL PYRROLIDINE

A six hundred grams of approximately 45% petroleum oil solution of N-tetraethylene pentamine polyisobutenylpyrrolidinedione, wherein the polyisobutenyl radical had a molecular weight of about 850, was blended with 800 ml. of ethyl ether. This blend was slowly added to a solution of 30 g. of lithium aluminum hydride in 2500 ml. of ethyl ether. The mixture was stirred under reflux for 12 hours after which 300 ml. of water was slowly added. The ether solution was washed with aqueous sodium hydroxide and centrifuged. The ether was removed by heating at 150° C. at an absolute pressure of 2 mm. of mercury. Analysis showed a nitrogen content of 1.87% and an absence of carbonyl groups.

EXAMPLE III.—PREPARATION OF 1-(3-DIMETHYLAMINOPROPYL)-3 - POLYISOBUTENYLPYRROLIDINE

Seven hundred grams of a 45% petroleum oil solution of N-dimethylaminopropyl polyisobutenyl pyrrolidinedione, the oil solution having a nitrogen content of 1.04%, was blended with 500 ml. of ethyl ether. This solution was slowly added to a solution consisting of 20 g. of lithium aluminum hydride in 750 ml. of ethyl ether. This solution was heated at reflux temperature overnight with agitation. Water was added, the solution filtered, dried over sodium sulfate, and the solvent removed by distillation to a temperature of 110° C. under vacuum. Analysis indicated a nitrogen content of 0.96%, and the absence of carbonyl groups.

EXAMPLE IV.—PREPARATION OF 1-(2-AMINOETHYL)-3-POLYISOBUTENYLPYRROLIDINE

Two hundred grams of a 34.9% petroleum oil solution of polyisobutenylsuccinic anhydride having a molecular weight of 1030 was blended with 300 ml. of xylene. This blend was dripped into 203 g. of warm, ethylenediamine with agitation. The mixture was distilled at 1 atm. to a pot temperature of 150° C. after which a vacuum was applied to the vessel and the temperature maintained at 170° C. for 2 hours.

On analysis, it was found that the nitrogen content was 0.90%, with the basic nitrogen content being 0.34%. This analysis showed that the product was an oil solution containing 34.5% active pyrrolidinedione material having a molecular weight of 1072.

The resulting pyrrolidinedione was reduced by slowly adding a solution consisting of 100 g. of the pyrrolidinedione dissolved in 100 ml. of dry ether to a stirred slurry of 3.5 g. of lithium aluminum hydride in 150 ml. of ether. This mixture was refluxed gently for 5 hours, treated with water, filtered, dried over potassium carbonate and heated to remove the solvent. On analysis, it was found that the total nitrogen content was 0.82%. Infrared analysis showed that no carbonyl groups were present.

EXAMPLE V.—PREPARATION OF 1-(6-AMINOHEXYL)-3-POLYISOBUTENYLPYRROLIDINE

The pyrrolidinedione was first prepared by reacting 430 g. of an oil solution (35%) of polyisobutenyl succinic anhydride (1030 mol wt.) with 350 g. of 1,6-hexanediamine. The solution was heated to 170° C. at an absolute pressure of 1 mm. of mercury to remove the excess diamine. The pyrrolidinedione was reduced by diluting with ether and dripping the ether solution into a dispersion of 15 g. of lithium aluminum hydride in 500 ml. of ether, followed by treatment in the manner set forth hereinabove.

On analysis, the product was found to have a total nitrogen content of 0.88%.

Table I hereinbelow presents engine data obtained with lubricating oil compositions containing 7.3% of the oil solution of the pyrrolidine of Example II hereinabove.

The test was a Caterpillar 1–H engine test run for the period of 120 hours.

The "PD Nos." refer to the piston discoloration rating. After the engine test, the three piston lands are examined visually. To a piston skirt which is completely black is assigned a PD number of 800; to one which is completely clean, a PD number of 0; to those intermediate between completely black and completely clean are assigned PD numbers intermediate in proportion to the extent and degree of darkening.

The "GD Nos." refer to the percentage deposits in the piston ring grooves; a 0 evaluation being a clean groove; and a number of 100 being a groove full of deposits.

The base oil was a California SAE 30 base oil.

Table I

Additive, Wt. Percent	A	B
Pyrrolidine of Example II	0.0	3.5
Test Results:		
GD No.	[1] 30	31
PD No.	800, 800, 800	295, 75, 80

[1] These test results were obtained in a Caterpillar L–1 test under the MIL–L–2104 conditions. Thus, under the more severe supplement–1 conditions, the GD No. would be considerably higher.

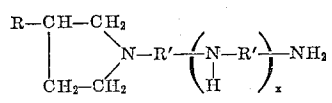
In addition to the pyrrolidines described hereinabove, the lubricating oil compositions may contain other detergents, rust inhibitors, corrosion inhibitors, pour point depressants, oiliness agents, oxidation inhibitors, etc.

We claim:

1. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 0.1% to 30% by weight, of 1-aminoalkyl-3-alkenyl pyrrolidine wherein the alkenyl radical has from 30 to 200 carbon atoms and the alkyl radical has from 2 to 6 carbon atoms.

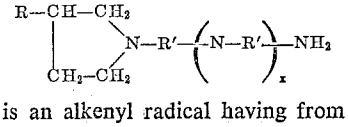
2. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 0.25% to 5% by weight, of 1-aminoalkyl-3-alkenyl pyrrolidine wherein the alkenyl radical has from 30 to 200 carbon atoms and the alkyl radical has from 2 to 6 carbon atoms.

3. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 0.1% to 30% by weight of an N-aminoalkyl-pyrrolidine of the formula



wherein R is an alkenyl radical having from 30 to 200 carbon atoms, R′ is a divalent alkylene radical having from 2 to 4 carbon atoms, and x is a number from 0 to 6.

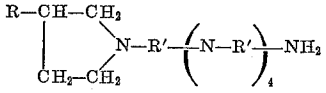
4. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 0.1% to 30% by weight of an N-aminoalkyl-pyrrolidine of the formula



wherein R is an alkenyl radical having from 30 to 200

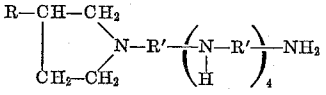
carbon atoms, R' is a divalent alkylene radical having 2 carbon atoms, and x is a number from 0 to 6.

5. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 0.1% to 30% by weight of an N-aminoalkyl-pyrrolidine of the formula



wherein R is an alkenyl radical having from 30 to 200 carbon atoms, and R' is a divalent radical having 2 carbon atoms.

6. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity, and from 0.25% to 5% by weight of an N-aminoalkyl-pyrrolidine of the formula

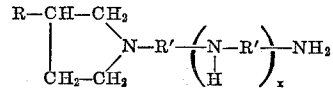


wherein R is an alkenyl radical having from 30 to 200 carbon atoms, and R' is a divalent radical having 2 carbon atoms.

7. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and from 0.1% to 30% by weight of 1-(triethylenetetraminoethyl)-3-polyisobutenyl pyrrolidine, wherein said polyisobutenyl radical contains from 30 to 200 carbon atoms.

8. A lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and from 0.1% to 30% by weight of 1-(3-dimethylaminopropyl)-3-polyisobutenylpyrrolidine, wherein said polyisobutenyl radical contains from 30 to 200 carbon atoms.

9. As a novel compound, an N-aminoalkylpyrrolidine of the formula



wherein R is an alkenyl radical having from 30 to 200 carbon atoms, R' is a divalent alkylene radical having from 2 to 4 carbon atoms and x is a number from 0 to 6.

10. As a novel compound, 1-(3-dimethylaminopropyl)-3-polyisobutenylpyrrolidine, wherein said polyisobutenyl radical contains from 30 to 200 carbon atoms.

References Cited by the Examiner

UNITED STATES PATENTS

3,018,250	1/62	Anderson et al.	252—51.5
3,083,139	3/63	Aspergren	260—313

DANIEL E. WYMAN, *Primary Examiner.*

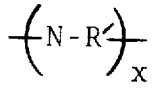
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,182,024 May 4, 1965

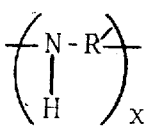
Frank A. Stuart et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

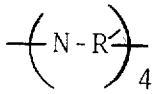
Column 2, line 22, for "carbon times" read -- carbon atoms --; column 4, lines 70 to 75, for that portion of the formula reading



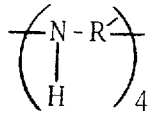
read



column 5, lines 7 to 10, for that portion of the formula reading



read



Signed and sealed this 16th day of November 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents