Patented July 4, 1950 2,514,017

UNITED STATES PATENT OFFICE

2,514,017

LUBRICANT

Aaron Wachter and Nathan Stillman, Berkeley, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application August 31, 1948, Serial No. 47,132

9 Claims. (Cl. 252—51.5)

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This invention relates to novel lubricating compositions. More specifically, this invention pertains to lubricants, such as mineral lubricating oils, synthetic lubricants of hydrocarbon and/or non-hydrocarbon origin, and the like, containing therein an additive having the property, inter alia, of reducing the combustion chamber deposits in internal combustion engines.

The deleterious effects of combustion chamber deposits in internal combustion engines are well known. For example, in spark ignition internal combustion engines, especially those operating on gasolines containing tetra-ethyl lead, deposits are formed which adhere to the various parts, such as the spark plugs, valve stems, piston crown, and the like, of the engine which come in contact with the combustion products of such fuels (gasolines), resulting in failure or deterioration, or both, of the affected parts. Scavenging agents, such as ethylene dibromide, normally added to leaded fuels, aid in preventing such deposition, but no such agent is known which even substantially solves the deposition problem. Engines which operate on non-leaded fuels, such as Diesel engines, also suffer from deposition (of the products of combustion) on the various parts of the engine, especially in the combustion chamber. Although the nature of the deposits varies according to the fuel composition employed, e. g., in spark ignition internal combustion engines operating on leaded gasoline the deposits contain a substantial portion of lead compounds, while in spark ignition internal combustion engines operating on non-leaded gasoline, and in compression ignition engines, such as Diesel engines, the deposits are largely carbonaceous in nature, the deleterious effects of all types of these deposits are recognized. The use of scavenging agents, as above-mentioned, which at best are inadequate, the use of special cleaning solvents, e. g., by flooding the combustion chambers therewith, and mechanical means, such as scraping, both of which latter methods require that the engine be idle, are the chief methods used until now for combatting combustion chamber deposits.

An object of this invention is to provide lubricating compositions which eliminate, or at least materially inhibit and/or reduce, the combustion chamber deposits of internal combustion engines. Another object is to provide lubricating compositions which decrease lacquer formation, ring sticking, and bearing corrosion. Other objects and their achievement in accordance with the present invention will be apparent from the following specification.

It has now been found that the incorporation in lubricants of compounds having a nitroso group attached to a nitrogen atom which in turn is attached to two hydrocarbon radicals eliminates, or at least materially reduces, combustion chamber deposits of internal combustion engines, and possesses other advantages, as hereinafter more fully described.

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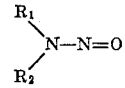
The compounds to be incorporated in lubricants to form the lubricating compositions of the present invention may be illustrated by the general formula:



wherein R_1 and R_2 are hydrocarbon radicals. Suitable radicals include, for example, alkyl, alkenyl, aralkyl, aryl, alicyclic and cyclo-olefinic radicals, such as the methyl, ethyl, propyl, isopropyl, normal butyl, secondary butyl, tertiary butyl, hexyl, iso-octyl, dodecyl, cetyl, stearyl, trimethyl octadecyl, allyl, methallyl, crotyl, oleyl, cyclopentyl, methyl cyclopentyl, cyclohexyl, isopropyl cyclohexyl, endomethylene cyclohexyl, cyclopentenyl, cyclohexenyl, phenyl, tolyl, xylyl, butyl phenyl, naphthyl, anthryl, and the like. R_2 may be the same or different from R_1; likewise, R_1 and R_2 may be connected to form a ring, together with the nitrogen atom which is also attached to the nitroso group.

Preferably, the present compounds are those wherein the total number of carbon atoms in both R_1 and R_2 is from about 5 to about 40, and preferably from 6 to about 20. Dicyclohexyl nitrosamine, illustrates such a compound, and when incorporated in a lubricant, forms therewith a preferred lubricating composition of the present invention. Other compounds which illustrate the additives of the present invention are di-isopropyl nitrosamine, di-n-butyl nitrosamine, di-n-propyl nitrosamine, diisopropyl nitrosamine, methylpentyl nitrosamine, methylcyclohexyl nitrosamine, diphenyl nitrosamine, bis(3,3,5-trimethyl-cyclohexyl) nitrosamine, methylbenzyl nitrosamine, allylbutyl nitrosamine, n-propylcyclohexenyl nitrosamine, and the like.

As above stated, it is essential to the success of the present invention that additives incorporated in lubricants to form the lubricating compositions of the present invention have a nitroso group attached to a ntirogen atom which in turn is attached to two hydrocarbon radicals. Thus, while there is relatively a wide latitude of choice in the selection of the radicals, the limitation being that the total number of carbon atoms in the molecule be at least about 5 and not more than about 40, they must be attached to a

$$=N—N=O$$

group in order to achieve the advantages of the present invention.

In preparing the compositions of the present invention one or more of the above-described compounds is incorporated in a liquid lubricant which will generally have a minimum boiling point of about 700° F. and a viscosity of at least about 100 Saybolt units at 100° F., and preferably higher, such as a mineral lubricating oil,

synthetic lubricant of hydrocarbon or non-hydrocarbon origin, and the like. Preferably, the present additives are dissolved in the lubricating oil. In order to impart a substantial oil solubility to the present compounds, the total number of carbon atoms in R_1 and R_2 of the above general formula is preferably at least 5, and preferably the total number is less than about 40. However, the present nitroso compounds may be dispersed or emulsified in the lubricant where necessary or desirable, in which case emulsifying agents, such as triethanolamine oleate, sodium oleate, the alkali metal sulfonates, and the like, may be employed if desired. Solutizers may also advantageously be employed in some instances. The quantity of the present additives to be incorporated in lubricants may be varied between about .001% and about 5% by weight, and good results obtained therewith, but preferably from about 0.01% to about 0.3% by weight is employed, since excellent results are economically obtained therewith. However, larger or smaller amounts of the additive, or mixtures thereof, may also be used.

Other additives which impart special properties to the lubricating composition may be incorporated in the present compositions where desirable. For example, pour point depressants, viscosity index improvers, oiliness carriers, and the like, may be incorporated in the compositions of the present invention without adversely affecting the action of the additives of the present invention, and the beneficial effects of such additional additives are obtained.

The following examples illustrate the compositions and process of engine operation in accordance with the present invention, which is not to be considered as limited thereby.

Example I

Various quantities of dicyclohexyl nitrosamine were dissolved in a mineral lubricating oil of S. A. E. grade 60. These compositions were tested in a Lauson supercharged engine (spark ignition, liquid cooled engine of 2.600 inch bore and 2½ inch stroke) operated at 2050 R. P. M. under a load of 5.0 B. H. P. for 10 hours on a 100 octane leaded gasoline. The following results, as compared to those obtained with the same oil without the additive, were obtained:

With the lubricating oil containing 0.03% by weight of dicyclohexyl nitrosamine deposits at the top ring groove were reduced by 25%, and lacquer on the piston skirt (the area below the piston rings in contact with the walls of the combustion chamber) was decreased by about 13%; lacquer on the piston undercrown was light and covered only about 25% of the total area, as compared to 100% of the area covered with a medium lacquer deposit observed in the absence of the additive. The combustion chamber deposits, as indicated by the deposition on the piston crown, was greatly decreased by the presence of the additive in the oil, and the small amount of deposits present were smooth and soft, instead of being rough, hard and uneven, as observed when operating on the same oil without the additive.

With the lubricating oil containing 0.1% by weight of dicyclohexyl nitrosamine, substantially similar results as the above were obtained. Especially notable, however, was the reduction of combustion chamber deposits.

Example II

Dicyclohexyl nitrosamine, 0.1% by weight, was dissolved in an S. A. E. grade 30 lubricating oil, and the resulting composition tested in a Caterpillar 4 cylinder, liquid cooled, Diesel engine having a bore of 4¼ inches and a stroke of 5½ inches operating at 1400 R. P. M. for 120 hours on a regular Diesel fuel.

Bearing weight loss, as compared to the loss when operating on the same lubricating oil without the additive, was reduced by 87.5%. The general engine cleanliness was greatly improved by the presence of the additive.

Example III

Example I was repeated using as the lubricant an S. A. E. grade 60 oil containing 0.25% by weight of the calcium salt of the condensation product of an alkylphenol and formaldehyde, calculated as the sulfate ash, and 0.05% by weight of the calcium salts of oil soluble petroleum sulfonic acids, calculated as the sulfate ash, and the same lubricating composition containing 0.1% by weight of dicyclohexyl nitrosamine.

Results were substantially as described for Example I, the reduction in combustion chamber deposits observed when employing the oil containing dicyclohexyl nitrosamine being especially marked.

Example IV

The same lubricating compositions of Example III were tested in a Franklin aircraft 4 cylinder, spark ignition, air cooled engine, having a 4 inch bore and 3½ inch stroke, and operated at 2200 R. P. M. with a load of 37 B. H. P. for 50 hours on an 80 octane grade leaded fuel.

Combustion chamber deposits, without the presence of dicyclohexyl nitrosamine, were heavy, and were greatly reduced when the oil containing dicyclohexyl nitrosamine was employed. As further indicative of this beneficial effect, without the presence of dicyclohexyl nitrosamine in the lubricant the spark plugs became fouled in 7 hours, while with the oil containing the additive no fouling was observed over the entire time of the run, 50 hours.

Example V

Dicyclohexyl nitrosamine, 0.1% by weight, was dissolved in an S. A. E. grade 30 lubricating oil, and the resulting composition tested in a Chevrolet 6 cylinder, liquid cooled, spark ignition engine having a bore of 3½ inches and a stroke of 3¾ inches, operating at 2500 R. P. M. under a load of 45 B. H. P. for 40 hours on a 76 octane leaded gasoline.

In addition to other advantages, such as a significant decrease in combustion chamber deposits, ring wear was reduced from 1.342 mg. per hour to 0.60 mg. per hour by the presence of dicyclohexyl nitrosamine in the lubricant.

Example VI

Comparative data were obtained with different lubricating compositions on a CUE (Wright cylinder) spark ignition, air cooled engine having a bore of 6.125 inches and a stroke of 6.875 inches, operating at 1800 R. P. M. for 100 hours on a 100 octane leaded gasoline. Both lubricants were S. A. E. grade 60 oil, one containing 0.25% by weight of the calcium salt of the condensation product of an alkylphenol and formaldehyde, calculated as the sulfonate ash and 0.05% by weight of the calcium salts of oil soluble petroleum sulfonic acids, calculated as the sulfate ash, and the same lubricating composition containing 0.1% by weight of dicyclohexyl nitrosamine.

By operation with the lubricant containing the dicyclohexyl nitrosamine, as compared to the same lubricant minus this additive, lacquer deposition on the piston was decreased by 15%, thereby giving a substantially cleaner piston, combustion chamber deposits as indicated by deposition in the top ring groove was reduced by 37%, and combustion chamber deposition as visually observed was substantially less, and the deposits which formed were of a soft, smooth character, as compared to the hard, uneven and brittle deposits otherwise obtained.

Example VII

In order to further illustrate the advantages of the present invention, Example I was repeated substituting the following nitrosamines at a concentration of 0.1% by weight, in place of dicyclohexyl nitrosamine: N-nitroso diphenylamine, diisopropyl nitrosamine and N-nitroso-di-(1,3-dimethylbutyl) amine. Although the advantageous results described in Example I were generally observed, the compounds were especially efficacious in reducing combustion chamber deposits.

Other additives which have a nitroso group attached to a nitrogen atom which in turn is attached to two hydrocarbon radicals, as defined and illustrated hereinbefore, may be substituted in the above examples for the various nitrosamines therein employed, which latter nitrosamines represent preferred materials selected to illustrate the present invention, and under substantially the same operating conditions results comparable to those described in the above examples are obtained.

In the above examples, a significant and unobvious advantage obtained by engine operation in accordance with the present invention is the decrease in deposition in both spark ignition engines operating on leaded fuels, and in compression ignition engines operating on non-leaded fuels, as demonstrated in the above examples. A further advantage is the change in properties of the combustion chamber deposits from a rough, hard, and uneven deposit to a soft, smooth deposit, caused by the presence in the lubricant of an additive containing a nitroso group attached to an organic radical through a nitrogen atom. This latter effect is of considerable importance. Thus, the hard deposit tends to become fused, heated to red heat, and by retaining the heat through the engine cycle tends to cause pre-ignition of the fuel in the subsequent cycles, whereas the soft deposit does not so tend to cause pre-ignition.

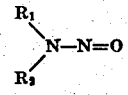
In order to demonstrate specificity of the present class of lubricant additives, Example I was repeated using 0.1% by weight of dicyclohexyl amine in place of the dicyclohexyl nitrosamine. No reduction in combustion chamber deposits over the oil containing no additive was observed, while a heavier lacquer coating was formed on the piston skirt.

The foregoing examples demonstrate the surprising reduction of combustion chamber deposits, among the other advantages, obtained in accordance with the present invention, by incorporating into lubricants for internal combustion engines only relatively small amounts of compounds having a nitroso group attached to a nitrogen atom which in turn is attached to an organic radical. The use of the present lubricating compositions in the operation of internal combustion engines constitutes a new process for the operation thereof, which process is within the scope of the present invention.

The present application is a continuation-in-part of the copending application Serial No. 663,608, filed April 19, 1946.

We claim as our invention:

1. A lubricant comprising a predominant amount of a mineral lubricating oil and from about 0.001% to about 5% by weight of a compound having the formula



wherein R_1 and R_2 are hydrocarbon radicals having a total of from 6 to about 20 carbon atoms.

2. A lubricant comprising a predominant amount of a mineral lubricating oil having a minimum boiling temperature of about 700° F. and from about 0.01% to about 0.3% by weight of dicyclohexyl nitrosamine.

3. A lubricant comprising a predominant amount of a mineral lubricating oil and from about 0.001% to about 5% by weight of dicyclohexyl nitrosamine.

4. A lubricant comprising a predominant amount of a mineral lubricating oil having a minimum boiling temperature of about 700° F. and from about 0.01% to about 0.3% by weight of diisopropyl nitrosamine.

5. A lubricant comprising a predominant amount of a mineral lubricating oil and from about 0.001% to about 5% by weight of diisopropyl nitrosamine.

6. A lubricant comprising a predominant amount of a mineral lubricating oil having a minimum boiling temperature of about 700° F. and from about 0.01% to about 0.3% by weight of N-nitroso diphenylamine.

7. A lubricant comprising a predominant amount of a mineral lubricating oil and from about 0.001% to about 5% by weight of N-nitroso diphenylamine.

8. A lubricant comprising a predominant amount of a mineral lubricating oil and from about 0.001% to about 5% by weight of an N-nitroso - di(aliphatic hydrocarbon) secondary amine containing a total of from 6 to about 20 carbon atoms.

9. A lubricant comprising a predominant amount of a mineral lubricating oil and from about 0.001% to about 5% by weight of an N-nitroso - di(saturated hydrocarbon) secondary amine containing a total of from 6 to about 20 carbon atoms.

AARON WACHTER.
NATHAN STILLMAN.

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