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HYDROCARBON SUBSTITUTED POLYCYANO-TETRAHYDROFURAN LUBRICATING OIL DETERGENTS

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U.S. Cl. 252—51.5 4 Claims

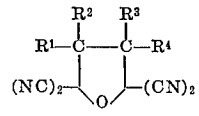
ABSTRACT OF THE DISCLOSURE

Aliphatic hydrocarbon substituted polycyanotetrahydrofurans are provided as lubricating oil detergents.

This invention concerns novel cyano substituted tetrahydrofuran derivatives which find use as detergents in lubricating oils.

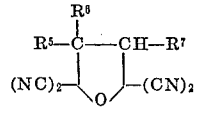
A development of major importance in the lubricating oil field has been the introduction of ashless detergents, that is, metal free compounds which are capable of reducing varnish and sludge deposits in internal combustion engines. An important advantage of these ashless detergents is the avoidance of the ash formed by the metal salt detergents on decomposition. Thus, valve and combustion chamber deposition with accompanying octane requirement increase can be minimized through their use.

It has now been found that lubricating oil detergents are provided by compositions of the formula:



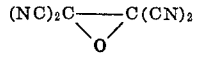
wherein R^1 to R^4 are hydrogen or aliphatic hydrocarbon having a total of from 30 to about 400 carbon atoms, more usually 30 to 300 carbon atoms, and may be aliphatically saturated or unsaturated.

For the most part, the compositions will have the following formula:



wherein at least one of R^5, R^6 and R^7 is aliphatic hydrocarbon while the other two may be hydrogen or aliphatic hydrocarbon, the total number of carbon atoms of R^5, R^6 and R^7 being in the range of 30 to 300, more usually in the range of 50 to 200. Usually, two of R^5, R^6 and R^7 will be hydrogen and/or lower alkyl.

The compositions of this invention may be readily prepared by contacting an aliphatic hydrocarbon olefin with tetracyanoethylene oxide which has the following formula:



The olefins which find use may be naturally occurring or synthetic straight chain, but preferably branched chain. Usually, the desired olefins can be obtained by polymerizing lower molecular weight olefins to a high molecular weight olefinic product.

Illustrative olefins include ethylene, propylene, butene-1, isobutylene, 4-methylpentene-1, either individually or in combination. The preferred olefins are propylene and isobutylene, i.e., olefins of from 3 to 4 carbon atoms.

The reaction is carried out by contacting the tetracyanoethylene oxide and olefin in an inert medium at elevated temperatures. The temperature is generally in the range of about 50° C., to 150° C. Depending on the temperature, the reaction time may vary from 1 hour to 24 hours. The ratio of the reactants is generally approximately stoichiometric. An inert solvent is usually used, either an aromatic hydrocarbon or a halohydrocarbon, e.g., toluene, 1-bromo-2-chloroethylene, etc.

The reaction product is readily obtained by removing the volatile materials *in vacuo,* dissolving the residue in inert aliphatic hydrocarbon, e.g., hexanes, and then extracting the hydrocarbon solution with an alkanol, e.g., ethanol. After drying the hydrocarbon layer, the volatile materials are removed and the product obtained.

The lubricating fluids (hereinafter referred to as oils) which are combined with the detergent compounds can be derived from natural or synthetic sources. Oils generally have viscosities of from about 35 to 50,000 Saybolt Universal Seconds (SUS) at 100° F. Among natural hydrocarbonaceous oils are paraffin base, naphthenic base, asphaltic base and mixed base oils. Illustrative of the synthetic oils are: hydrocarbon oils, such as polymers of various olefins; and alkylated aromatic hydrocarbons; and nonhydrocarbon oils, such as polyalkylene oxides, aromatic ethers, carboxylate esters, phosphate esters, and silicon esters. The preferred media are the hydrocarbonaceous media, both natural and synthetic.

The above oils may be used individually or together, whenever miscible or made so by the use of mutual solvents.

When being used in an internal combustion engine, the detergent will generally be compounded with the lubricating oil in amounts of at least about one weight percent and usually not more than 20 weight percent, more usually in the range of about 1.5 to 15 weight percent. The detergents, however, can be prepared as concentrates due to their excellent compatibility with oils. As concentrates, the compounds of this invention will generally range from about 20 to 70 weight percent of the total composition.

Usually included in the oils are other additives, such as extreme pressure agents, rust inhibitors, antioxidants, oiliness agents, foam inhibitors, viscosity index improvers, pour point depressants and occasionally other detergents. Usually, these will be present in the range from about 0.01 to 10 weight percent, more usually from about 0.5 to 5 weight percent of the composition; generally, each of the additives will be present in the range from about 0.01 to 5 weight percent of the composition.

A preferred aspect in using the detergent containing lubricating oil compositions of this invention is to include in the oil from about 1 to 50 mM./kg. of an O,O-dihydrocarbyl phosphorodithioate, wherein the hydrocarbyl groups are from about 4 to 30 carbon atoms. The remaining valence may be satisfied by zinc, a polyalkyleneoxy or a third hydrocarbyl group. (Hydrocarbyl is an organic radical composed solely of carbon and hydrogen.)

The following example is offered by way of illustration and not by way of limitation.

Example I (66-5)

Into a reaction flask was introduced 35 g. of polyisobutylene (0.03 mole) and 5 g. of tetracyanoethylene oxide (0.035 mole) and toluene added to form a 50 weight percent solution. The mix was refluxed in an inert atmosphere for 10 hours.

At the end of this time, the volatile material was stripped off in vacuo, maintaining the temperature below 50° C. The residue was dissolved in about an equal weight of hexanes and ethanol added. Water was added, until separation of two layers became obvious. The water layer was then discarded, and the procedure repeated three times

until the water layer was virtually colorless. The organic layer was then stripped of volatile materials in vacuo leaving the product. Analysis: Percent N, 2.96 (indicates some unreacted polyisobutylene present). An infrared spectrum was consistent with the tetracyanotetrahydrofuran product.

In order to demonstrate the effectiveness of the compositions of this invention, the exemplary composition of Example I was tested in a modified FL–2 test procedure, as described in the June 21, 1948 report of the Coordinating Research Council. This test simulates automobile engine performance. A standard procedure requires the maintenance of a jacket temperature of 95° F. and a crankcase oil temperature of 155° F. at 2,500 r.p.m. and 45 brake horsepower for 40 hours (closely simulating the relatively "cold" engine conditions which are normally experienced in city driving). At the end of each test, the engine is dismantled and the amount of total sludge and varnish (rating of 0 to 100, no sludge and varnish being 100) and clogging of the rings and oil screen (rating of 0 to 100, no clogging being 0) is determined. The above test was modified by increasing the time for the test and periodically raising the oil sump temperature from 165° F. to 205° F. and the water jacket temperature from 95° F. to 170° F.

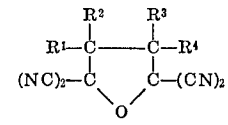
Using a Mid-Continent SAE 30 base stock, the exemplary detergent of Example I was employed at 1.56 weight percent concentration. Also included in the oil was 10 mM./kg. of zinc 0,0-di(alkyl dithiophosphate) (alkyl of from 4 to 6 carbon atoms) and 2 mM./kg. of zinc 0,0-di-(alkylphenyl) dithiophosphate (alkyl is polypropylene of from 12 to 15 carbon atoms). At the end of 60 hours, total sludge and varnish were rated at 50.7%, percent oil ring clogging at 83 and percent oil screen clogging at 20. With base oil, the engine is usually incapable of any further operation after about 12 hours.

It is evident from the above results that the compositions of this invention provide excellent detergency and lubrication in internal combustion engines. The presence of the cyano group also aids in providing some corrosion inhibition, particularly with lead copper bearings.

As will be evident to those skilled in the art, various modifications on this invention can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the following claims.

I claim:

1. A composition useful as a lubricating oil detergent, said composition having no more than about 400 carbon atoms and having the formula:



wherein at least one of R^1 to R^4 is aliphatic hydrocarbon having at least 30 carbon atoms and the remaining of R^1 to R^4 being selected from the group consisting of hydrogen and aliphatic hydrocarbon.

2. A composition according to claim **1**, wherein the total number of carbon atoms of R^1 to R^4 is in the range of 50 to 200.

3. A composition according to claim **1**, wherein at least one of R^1 to R^4 is derived from polyisobutenyl.

4. A lubricating oil composition having in an amount sufficient to provide detergency, a composition according to claim **1**.

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