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FUEL AND LUBE COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

The dispersant and detergent properties of lubricating oils and liquid hydrocarbon fuels such as gasoline are improved by addition of a small but effective amount of an N-hydrocarbyl-substituted nitrilotris ethylamine. The hydrocarbyl group is preferably a polyolefin group, such as a polybutene group, having a molecular weight of from about 300 to 20,000 more preferably from 500 to 2,000.

This application is a division of application Ser. No. 90,003, filed Nov. 16, 1970, now U.S. 3,700,598.

BACKGROUND

Detergent and dispersant properties of both fuels and lubricants have been improved by the addition of various materials. For example, high molecular weight alkenyl succinimides are described for this use in U.S. 3,172,892 and U.S. 3,202,678. Likewise, hydrocarbyl mono- and poly-amines are disclosed for this use in U.S. 3,438,757 and U.S. 3,275,554. The present additives are unique from those of the prior art in that they are built around the tertiary nitrogen atom in nitrilotris ethylamine.

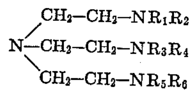
SUMMARY

An object of this invention is to provide improved fuels for use in internal combustion engines. A further object is to provide gasolines which, when used to operate an internal combustion engine, help maintain a fuel induction system of improved cleanliness. A further object is to provide a gasoline which will clean a dirty carburetor. Still another object is to provide a gasoline composition which leads to lower deposits in the induction system, especially in the area of the intake valves. Another object is to provide lubricating oils having improved properties. A further object is to provide mineral lubricating oils which tend to prevent the accumulation of dirt and sludge in internal combustion engines, especially those used in city-type driving. Still another object is to provide a lubricating oil which can be used in internal combustion engines for longer periods between drains.

The above and other objects are accomplished by providing N-hydrocarbyl-substituted nitrilotris ethylamines in which the hydrocarbyl groups have molecular weights of from about 300 to 20,000 and which, when added to lubricating oils or liquid hydrocarbon fuels, impart thereto dispersant and detergent properties.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A preferred embodiment of this invention is a dispersant-detergent composition having the formula:



$$N\left\{\begin{array}{l} CH_2-CH_2-NR_1R_2 \\ CH_2-CH_2-NR_3R_4 \\ CH_2-CH_2-NR_5R_6 \end{array}\right.$$

wherein R_1, R_2, R_3, R_4, R_5 and R_6 are independently selected from the group consisting of hydrogen and hydrocarbyl groups having an average molecular weight of from about 300 to 20,000 such that at least one of R_1, R_2, R_3, R_4, R_5 and R_6 is selected from said hydrocarbyl groups.

From one to six of the R groups bonded to nitrogen may be hydrocarbyl groups. Preferably, there are from about one to three high molecular weight hydrocarbon groups bonded to nitrogen. In a further preferred embodiment the hydrocarbon groups are substantially saturated aliphatic hydrocarbon groups. By "substantially saturated" is meant that less than 5 percent of the carbon-carbon bonds in the hydrocarbon group are olefinically or acetylenically unsaturated.

In a highly preferred embodiment these hydrocarbyl groups are polyolefin groups obtained by the polymerization of low molecular weight C_{2-5} olefins. They can be, for example, polyethylene, polypropylene, polybutene and polyamylene groups. More specifically, polypropylene and polybutene groups having an average molecular weight of from about 500 to 2,000 are exceptionally useful. By way of example, these polyolefin groups can have average molecular weights of 500, 600, 700, 800, 900, 1000, 1100, 1200 or 2000. In an especially preferred embodiment the hydrocarbyl groups are polyolefin groups having a molecular weight of from about 700 to 1200.

The additive compounds are readily prepared by known methods. The starting nitrilotris ethylamine (called herein NTEA) can be made by hydrogenating nitrilotriacetonitrile using, for example, a palladium or Raney nickel catalyst, which in turn can be made by known methods by reaction of formaldehyde, ammonia and hydrogen cyanide.

The hydrocarbyl group can be introduced into the NTEA nucleus by first halogenating the hydrocarbon group and then reacting it with the NTEA, causing hydrogen halide to be evolved and the hydrocarbon to become bonded to nitrogen. The number of hydrocarbon groups bonded to the NTEA can be controlled by adjusting the amount of hydrocarbyl halide employed and also the conditions of the reaction. Excess hydrocarbyl halide, high temperatures and long reaction periods all tend to introduce more hydrocarbon groups.

The halogenation of the hydrocarbon is conducted by known methods. Usually a halogen such as chlorine or bromine is merely bubbled into the stirred hydrocarbon at a temperature sufficient to cause the halogenation to proceed. Temperatures from 50 to 200° C. are useful. Halogenation aids such as UV light and metal halides (e.g., $FeCl_3$, $ZnCl_2$, $AlCl_3$, or BF_3) can be used, but are generally not required. Another method very useful when halogenating hydrocarbon containing a double bond such as the polyolefins is to react the olefinically unsaturated hydrocarbon with N-bromosuccinimide. This leads to introduction of a bromine atom allylic to the double bond, which is quite reactive and readily reacts with NTEA, leading to the desired additive. The halogenation should be conducted for a period such that about one halogen atom is substituted per hydrocarbon molecule. Excess halogenation is not required and should be avoided. However, a moderate amount of excess halogenation is not detrimental and usually leads to final additives containing some halogen. For the purpose of the present invention, the additives can contain up to about 10 percent halogen, although preferably they contain less than 2 or 3 percent.

The following examples illustrate the halogenation of polyolefin hydrocarbons useful in preparing the additives of this invention. All parts are by weight.

Example 1

A solution of 301 parts of Polybutene-24 (Chevron Chemical Company designation for polyisobutylene of molecular weight about 950) in 120 parts of benzene is placed in a vessel equipped with thermometer, stirrer, gas inlet tube and condenser. The solution is heated to about 73° C. and 22.7 parts of chlorine gas bubbled through over a period of about one hour.

The reaction vessel is then flushed with nitrogen gas for one hour. The solution is filtered and the solvent removed by vacuum distillation. The yield is 312 parts of polyisobutyl chloride. The product is an orange-colored viscous liquid, which on analysis contains 3.55 percent chlorine.

During the course of the chlorination of the polyisobutylene, hydrogen chloride was evolved and trapped. Analysis showed that one mole of hydrogen chloride was produced for every mole of chlorine consumed. This is positive evidence that the chlorination was a substitution rather than an addition reaction.

Example 2

A reaction vessel fitted with a thermometer, stirrer and condenser is charged with 94.1 parts of Polybutene-24, 17.8 parts of N-bromo succinimide and 200 parts of benzene. This mixture is refluxed for about 30 minutes. The mixture is then cooled and the solution filtered. The solvent is stripped and the residue then redissolved in hexane. This solution is filtered and the solvent removed by vacuum distillation. A 99 percent yield of the polyisobutyl bromide is obtained as a dark brown viscous liquid. The bromine content of this product is 7.9 percent.

The above procedures are equally applicable to any of the polyolefins of molecular weights from 300 to about 20,000 that might be used in preparing the present additives.

The following examples illustrate the halogenation of aliphatic hydrocarbons obtained from paraffins.

Example 3

In a reaction vessel is placed 975 parts of a paraffin wax having an average molecular weight of 325. This wax is heated to 100° C. and then chlorine is bubbled through the wax for one hour. The progress of the chlorination is followed by measuring the hydrogen chloride evolved. After 3.1 mole parts of hydrogen chloride have evolved, the chlorination is terminated.

The hydrocarbyl halides are reacted with the NTEA by merely mixing them together and heating the mixture. Generally, excess NTEA is employed. Good results are obtained using from about 0.3 to 20 moles of NTEA per mole of hydrocarbyl halide. The hydrocarbyl halide reacts with the reactive hydrogens on the primary amine groups of the NTEA, causing hydrogen halide to evolve and the hydrocarbyl group to bond to the nitrogen atom. A useful temperature range for this reaction is from about 50 to 250° C., and especially from about 70 to 150° C.

The following example serves to illustrate the reaction of a hydrocarbyl halide with NTEA to form the detergent-dispersant additives of this invention.

Example 4

In a reaction vessel is placed 950 parts of chlorinated polybutene prepared in Example 1 and 300 parts of NTEA. The mixture is heated to 75° C. and stirred while slowly raising the temperature to 100° C. Stirring is continued at 100° C. for 8 hours, and then the mixture is cooled and diluted with 2,000 parts of toluene. The solution is washed first with dilute (5%) aqueous caustic and then with water and the toluene and unreacted NTEA distilled out at reduced pressure. The viscous product remaining is an effective ashless dispersant for lubricating oils and is also beneficial when added to gasoline in preventing carburetor and intake system deposits.

Example 5

In a pressure reaction vessel is placed 2,000 parts of xylene and 1,580 parts of a polypropylene bromide made by the reaction of bromine with polypropylene (molecular weight 1500) at 75° C. and having an average of 1.2 atoms of bromine per mole. Following this, 73 parts of NTEA are added. The vessel is sealed and heated to 200° C. while stirring. It is maintained at 200° C. for 2 hours and then cooled. It is washed with aqueous caustic and water, following which the xylene and other volatiles are distilled out by heating to 150° C. at 5 mm. Hg. The product remaining is a N-polypropyl-substituted NTEA that is effective as a gasoline detergent and lube oil dispersant.

The foregoing examples serve to illustrate the simple manner in which the highly effective additives of this invention are prepared. Variations of the above general procedure to produce other related additives of this invention will be apparent.

The additives of this invention are useful dispersants in both mineral and synthetic lubricating oils. Examples of mineral lubricating oils include those refined from any crude oil such as Pennsylvania, midcontinent, Gulf Coast, California, and the like. The synthetic lubricants include both the hydrocarbon type and the other various types of synthetic lubricants. Hydrocarbon synthetic lubricants are generally polyolefin oligomers or alkylated aromatics. Examples are polybutene oligomers, styrene isobutylene copolymers, α-decene trimers, mixtures of alkylated benzenes from C_{12-26} olefins and having an average molecular weight of 450, and the like. These polyolefin oligomers are readily prepared from the appropriate olefin by standard oligomerization catalysts such as aluminum chloride, boron trifluoride diethyl aluminum chloride, ethyl aluminum sesquichloride, combinations of aluminum alkyls and metal salts such as diethyl aluminum chloride-titanium tetrachloride, ethyl aluminum sesquichloride-butyl vanadates, triethyl aluminum-zirconium iodides, and the like.

The alkylated aromatics are made by alkylating aromatics such as benzene, toluene, naphthalene, and the like, with olefin mixtures preferably containing C_{12-32} olefins. Catalysts such as $AlCl_3$ and BF_3 are effective and the average molecular weight of the product should be from about 300 to 600.

The additives are very effective in synthetic ester type lubricants including monoesters, diesters, complex esters, and the like. Some examples are C_{5-10} aliphatic monocarboxylic acid esters of trimethylolpropane, n-hexanoic ester of pentaerythritol, C_{5-9} aliphatic monocarboxylic esters of equal mole mixtures of trimethylolpropane and pentaerythritol, adipic acid diesters of C_{7-12} monohydric alkanols, complex esters formed by esterifying mixtures of polyols, dicarboxylic acids and monocarboxylic acids. For example, a useful complex ester is formed by condensing adipic acid, ethyleneglycol and a C_{5-10} mixture of aliphatic monocarboxylic acids. Another complex ester is formed from trimethylolpropane, adipic acid and C_{10-12} fatty alcohol mixtures. In essence, the complex esters are condensation products of polycarboxylic acids, polyols, and either monocarboxylic acids or monohydric alkanols, or both.

Other synthetic lubricants include the polyalkyl siloxanes, polyalkyl silicates, alkyl silicones, polyfluoro hydrocarbons, polyaryl ethers, polyalkoxy aryls, polyglycols, and the like.

The lubricant compositions are prepared by merely blending a dispersant amount of the additive with the oil. An effective amount is usually from about 0.1 to 5 weight percent, although more or less can be beneficially employed.

The lubricant compositions can include the other ingredients normally added to formulated lubricants. For example, mineral oil and synthetic hydrocarbon oil lubricants generally include zinc dialykydithiophosphates, calcium alkyl sulfonates, overbased calcium sulfonates containing colloidal calcium carbonate, calcium phenates, antioxidants such as 4,4′-methylenebis-(2,6-di-tert-butylphenol), 2,6-di-tert-butyl-α-dimethyl amino-p-cresol, phenylene diamines, barium phosphonates, polyalkyl methacrylate VI improvers, and the like. Synthetic ester formulations may include phosphate ester wear inhibitors such as tricresyl phosphate, phenyl dicresyl phosphate, and the like, antioxidants such as phenyl-β-naphthyl amine, phenylene diamines, phenothiazines, and the like, metal deactivators, silicone antifoam agents, and the like.

The following examples illustrate the preparation of some preferred lubricant compositions of this invention.

Example 6

In a blending vessel is placed 10,000 parts of solvent-refined midcontinent, neutral mineral oil (100 SUS). To this is added 100 parts of zinc diisobutyl dithiophosphate, 150 parts of overbased calcium alkaryl sulfonate (300 base number), 200 parts of polyaurylmethacrylate VI improver, and 50 parts of 4,4′-methylenebis-(2,6-di-tert-butylphenol). Following this, 35 parts of N-polybutyl nitrilotris ethylamine of Example 4 is added. The mixture is warmed to 50° C. and stirred until homogenous, giving a lubricant of good stability and excellent dispersant properties suitable for use in automotive engines.

Example 7

In a blending vessel is placed 10,000 parts of a hindered ester lubricant made by esterifying trimethylolpropane with a mixture of C_6 and C_8 n-aliphatic carboxylic acids. Following this, there is added 100 parts of phenyl-α-naphthyl amine, 100 parts of dioctyldiphenyl amine, 10 parts of 1-salicylalaminoguanidine, 300 parts of tricresyl phosphate, and .05 part of dimethyl silicone. Then, 300 parts of the N-polypropyl nitrilotris ethylamine of Example 5 is added. The mixture is warmed to 50° C. and stirred for 15 minutes. It is then filtered to give a synthetic ester lubricant suitable for use in turbines and turbojet engines.

The manner in which the additive is blended with the other lubricants mentioned is apparent from the foregoing examples.

The additives of this invention are also useful as detergents in liquid hydrocarbon fuels including distillate fuels, such as diesel fuel and liquid hydrocarbon fuels of the gasoline boiling range. Liquid hydrocarbon fuels of the gasoline boiling range are mixtures of hydrocarbons having a boiling range of from about 80° F. to about 430° F. Of course, these mixtures can contain individual constituents boiling above or below these figures. These hydrocarbon mixtures contain aromatic hydrocarbons, saturated hydrocarbons and olefinic hydrocarbons. The bulk of the hydrocarbon mixture is obtained by refining crude petroleum by either straight distillation or through the use of one of the many known refining processes, such as thermal cracking, catalytic cracking, catalytic hydroforming, catalytic reforming, and the like. Generally, the final gasoline is a blend of stocks obtained from several refinery processes. The final blend may also contain hydrocarbons made by other procedures such as alkylate made by the reaction of C_4 olefins and butanes using an acid catalyst, such as sulfuric acid or hydrofluoric acid.

Preferred gasolines are those having a Research Octane Number of at least 85. A more preferred Research Octane Number is 90 or greater. It is also preferred to blend the gasoline such that it has a content of aromatic hydrocarbons ranging from 10 to about 60 volume percent, an olefinic hydrocarbon content ranging from 0 to about 30 volume percent, and a saturate hydrocarbon content ranging from about 40 to 80 volume percent, based on the whole gasoline.

In order to obtain fuels having properties required by modern automotive engines, a blending procedure is generally followed by selecting appropriate blending stocks and blending them in suitable proportions. The required octane level is most readily accomplished by employing aromatics (e.g., BTX, catalytic reformate, or the like), alkylate (e.g., C_{6-9} saturates made by reacting C_4 olefins with isobutane using a HF or H_2SO_4 catalyst), or blends of different types.

The balance of the whole fuel may be made up of other components such as other saturates, olefins, or the like. The olefins are generally formed by using such procedures as thermal cracking, catalytic cracking and polymerization. Dehydrogenation of paraffins to olefins can supplement the gaseous olefins occurring in the refinery to produce feed material for either polymerization or alkylation processes. The saturated gasoline components comprise paraffins and naphthenes. These saturates are obtained from (1) virgin gasoline by distillation (straight run gasoline), (2) alkylation processes (alkylates) and (3) isomerization procedures (conversion of normal paraffins to branched chain paraffins of greater octane quality). Saturated gasoline components also occur in so-called natural gasoline. In addition to the foregoing, thermally cracked stocks, catalytically cracked stocks and catalytic reformates contain saturated components.

The classification of gasoline components into aromatics, olefins and saturates is well recognized in the art. Procedures for analyzing gasolines and gasoline components for hydrocarbon composition have long been known and used. Commonly used today is the FIA analytical method involving fluorescent indicator adsorption techniques. These are based on selective adsorption of gasoline components on an activated silica gel column, the components being concentrated by hydrocarbon type in different parts of the column. Special fluorescent dyes are added to the test sample and are also selectively separated with the sample fractions to make the boundaries of the aromatics, olefins and saturates clearly visible under ultraviolet light. Further details concerning this method can be found in "1969 Book of ASTM Standards," January 1969 edition, under the ASTM Test Designation D 1319–66T.

The motor gasolines used in formulating the improved fuels of this invention generally have initial boiling points ranging from about 80 to about 105° F. and final boiling points ranging from about 380 to about 430° F. as measured by the standard ASTM distillation procedure (ASTM D–86). Intermediate gasoline fractions boil away at temperatures within these extremes.

From the standpoint of minimizing atmospheric pollution to the greatest extent possible, it is best to keep the olefin content of the fuel as low as can be economically achieved as olefins reportedly give rise to smog-forming emissions, especially from improperly adjusted vehicular engines. Accordingly, in the preferred base stocks of this invention the olefin content will not exceed about 10 volume percent and most particularly preferred fuels will not contain more than about 5 percent olefins. Table I illustrates the hydrocarbon type makeup of a number of particularly preferred fuels for use in this invention.

TABLE I

Hydrocarbon blends of particularly preferred base fuels

	Volume percentage		
	Aromatics	Olefins	Saturates
Fuel:			
A	35.0	2.0	63.0
B	40.0	1.5	58.5
C	40.0	2.0	58.0
D	33.5	1.0	65.5
E	36.5	2.5	61.0
F	43.5	1.5	55.0
G	49.5	2.5	+48.0

It is also desirable to utilize base fuels having a low sulfur content as the oxides of sulfur tend to contribute an irritating and choking character to smog and other forms of atmospheric pollution. Therefore, to the extent it is economically feasible, the fuel will contain not more than about 0.1 weight percent of sulfur in the form of conventional sulfur-containing impurities. Fuels in which the sulfur content is no more than about 0.02 weight percent are especially preferred for use in this invention.

Utilization of non-hydrocarbon blending stocks or components in formulating the fuels of this invention is feasible and, in some instances, may actually be desirable. Thus, use may be made of methanol, tertiary butanol and other inexpensive abundant and non-deleterious oxygen-containing fuel components.

It will, of course, be understood that the hydrocarbon fuels used in the practice of this invention will be resistant to oxidative degradation on exposure to air. Through improvements and advances made in refining techniques there is no longer a necessity for relying heavily upon use of catalytically cracked or thermally cracked stocks which tend to be the most oxidatively unstable fuel components. Greater utilization of the more stable components (aromatics and saturates) is now possible and customary. Nevertheless, in any instance where the base fuel has insufficient storage stability in the presence of air, use will be made of an appropriate quantity of an antioxidant. This provides a gasoline of suitable stability for storage, transporation, and use.

The amount of the detergent added to the fuel should be at least sufficient to exert some detergent action in the fuel induction system. In other words, it should be a detergent amount. Detergent action is generally attained when the fuel contains from about 50–2000 p.p.m. (parts per mililon) of the new detergent, and more preferably, when it contains from about 100–1000 p.p.m.

The gasoline may contain any of the other additives normally employed to give fuels of improved quality, such as tetraalkyllead antiknocks including tetramethyllead, tetraethyllead, mixed tetraethyltetramethyl lead, and the like. They may also contain antiknock qualities of other agents such as cyclopentadienyl nickel nitrosyl, methylcyclopentadienyl manganese tricarbonyl, and N-methyl aniline, and the like. Antiknock promoters such as tert-butyl acetate may be included. Halohydrocarbon scavengers such as ethylene dichloride, ethylene dibromide and dibromo butane may be added. Phosphorus-containing additives such as tricresyl phosphate, methyl diphenyl phosphate, diphenyl methyl phosphate, trimethyl phosphate, and tris(β-chloropropyl)phosphate may be present. Antioxidants such as 2,6-di-tert-butylphenol, 2,6-di-tert-butyl-p-cresol, phenylenediamines such as N-isopropylphenylenediamine, and the like, may be present. Likewise, the gasoline can contain dyes, metal deactivators, or any of the additives recognized to serve some useful purpose in improving the gasoline quality.

A preferred embodiment of the invention is a liquid hydrocarbon fuel of the gasoline boiling range containing a detergent amount of the new detergent of this invention and from about 0.25 to 4 grams per gallon of lead as tetraethyllead or tetramethyllead. A still further embodiment of the invention is a liquid hydrocarbon fuel of the gasoline boiling range containing a detergent amount of the new detergent of this invention and from about 0.005 to 3, more preferably 0.005 to 0.5, gram of manganese per gallon as methylcyclopentadienyl manganese tricarbonyl.

A highly preferred embodiment of this invention is a liquid hydrocarbon fuel of the gasoline boiling range as previously described containing in addition to the detergent additive a small amount of a mineral oil. This embodiment is particularly advantageous in promoting the cleaning of intake valves and stems in spark ignited internal combustion engines. The amount of oil added can be any amount from about 0.05 to about 0.5 volume percent, based on the final gasoline. Although the oil adjuvant can be any of the well-known mineral oils including those obtained from Pennsylvania, midcontinent, Gulf-coast, or California crudes, the more preferred are the naphthenic mineral oils. The viscosity of the mineral oil can vary from about 100 to 2000 SUS at 100° F.

In another preferred embodiment a synthetic olefin oligomer is used in place of or together with the mineral oil adjuvant. These oligomers are prepared by the polymerization of aliphatic monoolefinic hydrocarbons containing from 2 up to about 32 carbon atoms, such as ethylene, propylene, butene, decene-1, eicosene-1, triacontene-1, and the like. These result in such adjuvants as polyethylene, polypropylene, polybutene, α-decene trimer, α-decene tetramer and mixtures of the proper average molecular weight. Useful polymerization catalysts include both the Lewis acid type such as aluminum chloride, boron trifluoride, etc., as well as the metal alkyl types such as triethyl aluminum, diethyl aluminum chloride, methyl aluminum sesquichloride, diethyl zinc, either alone or in combination with a metal salt modifier such as titanium tetrachloride or cobalt iodide. Means of carrying out the polymerization of the simple olefin monomers are well known.

The polymerization should be carried out until the olefin forms a normally liquid oligomer having an average molecular weight of from about 300 to 2000, especially 350–1500. The oligomers of this molecular weight range have the greatest effect in promoting the cleaning of intake valves when used in combination with a detergent of this invention.

In an especially preferred embodiment the polyolefin adjuvant is a normally liquid olefinic hydrocarbon having an average molecular weight of from about 350 to about 1500 and is made by the polymerization of a mixture of aliphatic monoolefins containing at least 12 carbon atoms. Preferably the monoolefins used to prepare this polyolefin adjuvant contain from about 12–32 carbon atoms and are predominantly alpha-olefins. More preferred olefin hydrocarbons are those obtained by polymerizing a mixture of even numbered, predominantly alpha-monoolefins having from 12 to about 32 carbon atoms using a Friedel-Crafts catalyst. Preferred Friedel-Crafts catalysts are aluminum chloride, aluminum bromide, and boron trifluoride. Preferred reaction temperatures are 20° C.–120° C. A most preferred polymerization process is carried out at temperatures ranging from about 40° C. to about 110° C., using an aluminum halide catalyst in the absence of any lower alkyl (C_1–C_6) monohalide.

These poly-C_{12+} olefin adjuvants are non-aromatic, normally liquid olefin hydrocarbons characterized by having an average molecular weight ranging from 350 to about 1500. By "normally liquid" is meant that the olefin hydrocarbon is fluid at room temperature. These olefin hydrocarbons include cyclic olefin hydrocarbons as well as branched chain and straight chain olefin hydrocarbons.

Although olefin hydrocarbons useful as adjuvants may contain only one carbon polyolefin, for example, triacontene (C_{30}), pentacontene (C_{50}), a C_{100} olefin, α-dodecene trimer, α-dodecane tetramer, and the like, preferred poly-C_{12+} olefins are made using mixtures of olefins having at least 16 or more and preferably at least 24 or more carbon atoms. The mixtures of olefins which make up these preferred olefin hydrocarbons may be obtained directly from commercial processes such as Ziegler catalyzed ethylene and/or propylene polymerization; dehydrohalogenation of suitable alkyl halides; the catalytic dehydrogenation of suitable paraffins, for example, wax cracked paraffins; or oligomerization of suitable olefins; or other similar processes.

Particularly preferred olefin hydrocarbon additives are those obtained by polymerizing non-aromatic, primarily alpha-monolefin mixtures having 8 or more, and preferably 12 or more, carbon atoms. By predominantly alpha is meant that more than 50 percent by weight of the monoolefin mixture has the alpha configuration.

The polymerization of these monoolefins can be effected with various catalyst systems. Useful polymerization procedures are disclosed, for example, in U.S. 2,620,-365; U.S. 3,206,523; U.S. 3,232,883; U.S. 3,252,771; U.S. 3,253,052; U.S. 3,259,668; U.S. 3,261,879; U.S. 3,322,848; U.S. 3,325,560; U.S. 3,330,883; U.S. 3,346,662; and U.S. 3,450,786. The olefin hydrocarbon products prepared using procedures such as those described in the patents listed are useful as adjuvants together with the detergents of this invention in gasoline provided that the product has the required average molecular weight, is normally liquid, and is non-aromatic in nature.

A most preferred normally liquid non-aromatic olefin hydrocarbon is the product obtained by polymerizing a mixture of even carbon numbered, predominantly alpha-monoolefins having from 12 to 32 carbon atoms using a Friedel-Crafts catalyst, preferably selected from aluminum chloride, aluminum bromide, and boron trifluoride, at reaction temperatures ranging from 0° C. to about 145° C. A most preferred polymerization is carried out in the absence of any lower alkyl (C_1–C_6) halide such as methylchloride, n-hexylchloride, isopropylchloride, ethylchloride, and the like, at temperatures ranging from 20° C.–110° C. $AlCl_3$ and $AlBr_3$ are most preferred catalysts.

The polymerization reaction is ordinarily carried out without the addition of any inert diluent. However, the polymerization can be carried out in the presence of an inert diluent, e.g., an alkane, if desired.

The polymerization reaction time is to a degree dependent on the monoolefin feed stream, the reaction temperature, the catalyst concentration, and the like. For example, when aluminum chloride is used as the catalyst, at a reaction temperature of 70° C. with an olefin feed containing C_{12}–C_{32} olefins, a 2-hour reaction time is sufficient. Thus, the reaction time can be adjusted as required to produce the olefin hydrocarbons of the proper molecular weight range to be useful in the present invention.

The preferred Friedel-Crafts catalysts are aluminum chloride, aluminum bromide, and boron trifluoride. The concentration of catalyst used may be varied. Generally, from about 2 percent to about 10 percent of the catalyst, based on the weight of monoolefin charged, can be used. About 5 percent of the catalyst, based on the weight of the olefin charged, is conveniently used.

The preferred monoolefins which can be polymerized using the Friedel-Crafts process described above are mixtures of acyclic monoolefin hydrocarbons having from about 12 to about 32 carbon atoms. These monoolefin mixtures are synthesized by methods known in the art. For example, they may be prepared by cracking wax paraffins; by catalytically dehydrogenating paraffinic hydrocarbons; or by polymerizing low molecular weight monoolefins, such as ethylene, using Ziegler-type catalysts. It is the general nature of these monoolefin preparations that mixtures of monoolefins are obtained. These monoolefin mixtures can vary widely in composition from 100 percent α-monoolefins, through intermediate mixtures, to 100 percent internal monoolefins; mixtures which contain 30 percent or more α-monoolefins are preferred. The range of carbon chain lengths in these mixtures can also vary considerably. Both branched and linear olefins can be present in these mixtures. Useful mixtures can also contain small amounts of monoolefins outside the C_{12}–C_{32} range. Mixtures in which α-monoolefins predominate are more preferred; by predominate is meant that more than 50 percent by weight of the olefin mixture is α-monoolefin. In addition to the monoolefins, the mixture can also contain small quantities of certain by-products (or co-product). The type of by-product or co-product found in the α-monoolefin mixtures will depend to a great degree on the method used to prepare the monoolefins. Thus, for example, if the monoolefin mixture is prepared by catalytic dehydrogenation of paraffins in the C_{12}–C_{32} range, the monoolefin mixture may contain some of the starting paraffin, while with Ziegler-catalyzed ethylene systems the by-product present in the monoolefin may be paraffins as well as higher molecular weight alkanols. Generally, the monoolefin mixtures containing these by-products can be used as such; provided the presence of the by-product does not adversely affect the Friedel-Crafts polymerization reaction and olefin hydrocarbon product.

Examples of useful monoolefin mixtures are those having the following monoolefin composition by weight: 30% C_{12}, 40% C_{14}, and 30% C_{16}; 10% C_{13}, 20% C_{14}, 25% C_{15}, 25% C_{16}, 15% C_{17} and 5% C_{18}; 2% C_9, 3% C_{10}, 5% C_{11}, 30% C_{12}, 35% C_{13}, 20% C_{14} and 5% C_{15}; 30% C_{12}, 30% C_{14} and 40% C_{16}; 1% C_8, 2% C_{10}, 15% C_{12}, 22% C_{14}, 24% C_{16}, 20% C_{18}, 10% C_{20}, 4% C_{22} and 2% C_{24}; 50% C_{22} and 50% C_{24}; 20% C_{26}, 60% C_{28} and 20% C_{30}; 5% C_{23}, 15% C_{24}, 30% C_{25}, 32% C_{26}, 10% C_{27} and 8% C_{28}; 11% C_{16}, 63% C_{18}, 20% C_{20} and 6% C_{22+}; 6% C_{26}, 15% C_{28}, 40% C_{30}, 36% C_{32} and 3% C_{34}, and the like.

Preferred mixtures of monoolefins contain even carbon numbered olefins ranging from about C_{12} to about C_{32} with an α-monoolefin content of 30 percent or more. These mixtures may contain small amounts of C_6, C_8 and C_{10} olefins as well as C_{34+} or higher olefins; as well as paraffin and alkanol by-products as described above.

More preferred mixtures of monoolefins are those containing even carbon numbered olefins, ranging from about C_{12} to about C_{32}; the olefins are predominantly α-monoolefins. These mixtures can also contain small amounts of C_6, C_8 and C_{10} olefins as well as C_{34} and higher olefins; as well as paraffin and alkanol by-products as described above.

Compositions of typical preferred monoolefin mixtures useful for Friedel-Crafts polymerization are listed in the following table. These preferred monoolefins will be designated herein as C_{12+} monoolefins or C_{12+} monoolefin mixtures.

TABLE II

C_{12} monoolefin mixtures

	A	B	C	C′ [2]
Olefin carbon No., percent by weight: [1]				
C_8–C_{10}	1.84	1.40	2.01	4.35
C_{12}	20.39	16.72	19.40	13.92
C_{14}	12.15	9.76	12.59	9.91
C_{16}	10.65	8.28	10.97	9.27
C_{18}	6.29	6.34	8.88	9.51
C_{20}	4.35	4.43	5.15	6.04
C_{22}	3.25	5.59	6.63	7.51
C_{24}	4.38	7.50	7.70	8.21
C_{26}	3.51	6.41	4.78	5.80
C_{28}	2.07	3.69	2.40	3.00
C_{30}	1.33	1.25	0.90	0.61
C_{32}		0.38	0.17	------
C_{34}		0.08	------	------
Total olefins, percent	70.21	72	81.58	78.13
Total paraffins, percent	18.30	28	18.42	21.87
Other by-products, percent	[3] 11.49	------	------	------
Olefin configuration, percent distribution: [4]				
α	69.7	60.6	------	60.1
Internal	30.3	39.3	------	39.9

[1] Vapor phase chromatographic analysis.

[2] For this mixture, VPC analysis was based on 91.11% recovered normalized. The mixture also contained by-product alcohols.

[3] Estimated.

[4] Nuclear magnetic resonance analysis.

A typical mixture of C_{12+} monoolefins has the followin general composition by weight: C_8–C_{10} olefins—3%, C_{12}–C_{18} olefins—39.2%, C_{20+} olefins—33.6%, C_8–C_{10} paraffins—2%, C_{12}–C_{18} paraffins—19.4%, C_{20+} paraffins—0.8%, alcohols—2%.

The more preferred monoolefin mixtures can also be treated with an isomerization catalyst prior to being polymerized. The isomerization effected in this case is primarily isomerization of the vinylidene type α-olefins to internal olefins. Thus, for example, isomerizing a more preferred C_{12+} olefin mixture containing 30% vinyl α-olefins, 40% vinylidene α-olefins, and 30% internal olefins using a suitable catalyst such as silica gel, activated alumina, and the like, the isomerized C_{12+} olefin will now contain 30% vinyl α-olefins, less than 40% vinylidene α-olefins and 30%+ internal olefins, the "+" indicating the amount of vinylidene olefin isomerized to internal olefin. Depending on the extent of vinylidene olefin isomerization, the resulting isomerized monoolefin mixture may contain (a) α-olefins predominantly, (b) internal olefins predominantly, or (c) an equal amount of α-olefins and internal olefins. In any event, such isomerized olefin mixtures containing 30% or more α-monoolefins are also useful to prepare the olefin hydrocarbons of the present invention.

The following examples will illustrate the preparation of preferred normally liquid olefin hydrocarbons having a molecular weight of from 350 to 1500 by Friedel-Crafts polymerization of mixtures of α-monoolefins of the type disclosed above. All parts are by weight unless otherwise indicated. The molecular weight of the olefin hydrocarbon products was determined by vapor phase osmometry.

Example 8

A vessel was flushed with nitrogen and then charged with 454 parts of a C_{12+} monoolefin mixture. The olefin mixture was cooled to 15° C.; 15 parts of aluminum chloride were added to this olefin mixture over a 3–4 minute period. The reaction mixture was then heated with stirring at 70° C. for 2 hours. The catalyst was then quenched by adding about 150 parts of a 10% HCl solution to the mixture. About 350 parts of hexane were added (to facilitate handling) and the diluted mixture was washed with water until the washings were acid free. The reaction mixture was then filtered through Celite. The filtrate was stripped of water and solvent under vacuum on a steam bath. The product obtained was 308 parts of a clear, yellow, very fluid liquid. The molecular weight of this product was 368.

An analogous product is obtained when the reaction of Example 8 is carried out at 0° C. for 16 hours; at 145° C. for 30 minutes; or at 40° C. for 5 hours. Boron trifluoride is used with equal effectiveness in place of aluminum chloride in Example 8.

The gasoline detergent additives of this invention can be added directly to gasoline or they can be added in the form of a concentrate. Thus, another embodiment of the invention is a gasoline detergent concentrate containing an additive amount of a detergent of this invention and a diluent. The amount of detergent in the concentrate can vary from about 10–90 weight percent. A preferred concentration is from about 35–75 weight percent. The diluent serves to maintain the concentrate in a liquid form making it easy to handle and to meter into gasoline blending systems. Preferred diluents are hydrocarbons including both aliphatic and hydrocarbons such as hexane, heptane, octane, petroleum ether, kerosene, benzene, toluene, xylene, and the like, including mixtures thereof. A more preferred diluent is a higher boiling hydrocarbon such as a mineral oil or polyolefin oligomer. The advantage of using these higher boiling hydrocarbon diluents is that these higher boiling hydrocarbons also serve as the previously-described mineral oil or polyolefin adjuvants. Thus, a preferred concentrate contains from about 10–90 weight percent, preferably 35–75 weight percent, of the detergent in a mineral oil or polyolefin oligomer. When this concentrate is added to gasoline a fuel is provided which will maintain the entire induction system in a high degree of cleanliness.

Especially good results have been obtained when the hydrocarbon diluent employed in the concentrate is one of the previously-described polyolefin oligomers made by polymerizing an olefin or mixture of olefinic hydrocarbons containing about 12 or more carbon atoms, preferably from 12–32 carbon atoms, to produce a liquid olefin polymer having an average molecular weight of about 300–1500.

The detergent concentrate can contain other additives normally used with gasoline, forming an additive "package." For example, the concentrate can contain gasoline antioxidants such as 2,6-di-tert-butylphenol, mixtures of butylated phenol containing about 75 percent of 2,6-di-tert-butylphenol, 15 percent o-tert-butylphenol, N-isopropylphenylenediamine; phosphorus additives such as tricresylphosphate, trimethylphosphate, phenylidimethylphosphate, dimethylphenylphosphate, tris(β-chloropropyl) phosphate, and the like; antiknock promoters such as tert-butyl acetate; de-icers such as methanol, isopropanol, n-butanol, isobutanol; tetraalkyllead antiknocks such as tetraethyllead, tetramethyllead, redistributed tetraethyltetramethyllead, and the like; scavengers such as ethylene dichloride, ethylene dibromide, dibromobutanes, and the like; other antiknock agents such as methyl cyclopentadienyl manganese tricarbonyl, ferrocene, methyl ferrocene, cyclopentadienyl nickel nitrosyl, N-methylaniline, and the like; metal deactivators such as N,N'-disalicylidene-1,2-diaminopropane; dyes; corrosion inhibitors, and the like.

The concentrates of this invention are readily prepared by merely blending the ingredients until a homogenous solution is obtained. The following examples illustrate the preparation of some typical concentrates.

Example 9

To a blending vessel is added 1000 parts of the detergent product from Example 4 and 1000 parts of a naphthenic mineral oil. The mixture is warmed and stirred until homogenous, forming an additive concentrate useful for improving the detergent properties of gasoline.

Example 10

To a blending vessel is added 1000 parts of the detergent additive for Example 5 and 1500 parts of the olefin oligomer from Example 8. Then, 20 parts of a mixture of butylated phenols containing about 75 percent 2,6-di-tert-butylphenol are added. This mixture is stirred, forming a detergent package which also imparts antioxidant protection when added to gasoline.

The amounts of each ingredient in the foregoing compositions can be varied within the wide limits to provide the optimum degree of each property.

Gasoline compositions of this invention can be prepared by merely adding the detergent in the proper amount to the gasoline base stock and stirring until dissolved. Likewise, the detergent can be injected into the gasoline stream in an in-line blending system either alone or in combination with other additives such as tetraalkyllead antiknocks. Similarly, the additive concentrate can be added to gasoline, furnishing not only the detergent but also the adjuvant (mineral oil or olefin oligomer). If desired, the detergent and adjuvant can be separately added to the base gasoline.

The following examples serve to illustrate the manner in which gasoline compositions of this invention are made. In these examples the gasoline base stocks have the following composition and properties.

TABLE III

		Boiling range (° F.)		Composition, percent		
	RON	Initial	End point	Aromatics	Olefins	Saturates
Fuel:						
H	91	91	390	40	1.5	58.5
I	86	100	400	35	2	63
J	87	95	410	36.5	2.5	61
K	95	89	395	49.5	2.5	48
L	97	105	415	54	1.5	44.5
M	90	96	389	39	3	58
N	94	87	395	51	0.5	48.5

Example 11

In a blending vessel is placed 10,000 gallons of Gasoline H, 25 pounds of the detergent of Example 4, 100 pounds of the poly-C_{12+} olefin of Example 8, 96.5 pounds of tetraethyllead as a commercial antiknock fluid containing one theory of ethylene dichloride and 0.5 theory of ethylene dibromide, and 15.5 pounds of tricresylphosphate. The mixture is stirred until thoroughly mixed. The resultant gasoline is a premium grade gasoline with good detergent properties.

Example 12

In a blending vessel is placed 10,000 gallons of Gasoline L, 2.5 pounds of detergent of Example 5, and 50 pounds of a neutral mineral oil (viscosity 100 SUS at 100° F.). The mixture is stirred, resulting in an unleaded gasoline having good detergent properties.

Examples 13–22

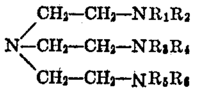
The above Examples 11 and 12 are repeated using each of Gasolines I, J, K, M and N.

Example 23

To a blending vessel is added 10,000 gallons of Gasoline I, 100 pounds of the additive package of Example 10, 84 pounds of tetraethyllead as a commercial antiknock fluid, and 4.8 pounds of trimethylphosphate. The mixture is stirred, giving a high quality gasoline of good detergent properties.

We claim:

1. A dispersant-detergent composition having the formula:



$$N\begin{cases} CH_2-CH_2-NR_1R_2 \\ CH_2-CH_2-NR_3R_4 \\ CH_2-CH_2-NR_5R_6 \end{cases}$$

wherein R_1, R_2, R_3, R_4, R_5 and R_6 are independently selected from the group consisting of hydrogen and hydrocarbyl groups having an average molecular weight of from about 300 to 20,000 such that at least one of R_1, R_2, R_3, R_4, R_5 and R_6 is selected from said hydrocarbyl groups.

2. A composition of claim **1** wherein said hydrocarbyl groups are substantially saturated aliphatic hydrocarbyl groups.

3. A composition of claim **2** wherein said hydrocarbyl groups are poly-C_{2-5} olefin groups.

4. A composition of claim **3** wherein said poly-C_{2-5} olefin group is a polypropylene group.

5. A composition of claim **4** wherein said polypropylene group has an average molecular weight of from 500 to 2,000.

6. A composition of claim **3** wherein said poly-C_{2-5} olefin group is a polybutene group.

7. A composition of claim **6** wherein said polybutene group has an average molecular weight of from about 500 to 2,000.

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