

- [54] **OLEFINIC KETONE IMINES AND OIL COMPOSITIONS CONTAINING THEM**
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Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 502,438, Oct. 22, 1965, abandoned.
- [52] U.S. Cl. **260/566 R**, 260/268 R, 260/934, 252/50, 44/73
- [51] Int. Cl. **C07c 119/00**
- [58] Field of Search 260/566 R, 268 R

References Cited

UNITED STATES PATENTS

2,129,615	9/1938	Calvert.....	260/566 R X
2,652,367	9/1953	Adelson	260/566 R X
3,018,193	1/1962	Cyba	260/566 R X
3,459,710	8/1969	Caiola et al.....	260/566 R X

OTHER PUBLICATIONS

House, "Modern Synthetic Reactions," pp. 94-95(1965).

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Attorney, Agent, or Firm—Byron O. Dimmick

[57] **ABSTRACT**

A multifunctional additive for an oil from the class consisting of gasoline, middle distillate petroleum fuels, mineral lubricating oils, and synthetic lubricating oils is prepared by reacting an aliphatic polyamine such as diethylene triamine, tetraethylene pentamine, and the like with an unsaturated ketone that has been prepared by the mild oxidation of a terminal olefin having from 12 to 250 carbon atoms. The reaction involves the formation of a Schiff base from the carbonyl group of the ketone and an amino group of the aliphatic polyamine. Modified products can be prepared by treating the unsaturated ketone with a sulfide of phosphorus, e.g., P₂S₅, or with a dihydrocarbyl dithiophosphoric acid prior to the step of reacting the ketone with the aliphatic polyamine.

6 Claims, No Drawings

OLEFINIC KETONE IMINES AND OIL COMPOSITIONS CONTAINING THEM

This application is a continuation-in-part of Ser. No. 502,438, filed Oct. 22, 1965 now abandoned.

FIELD OF THE INVENTION

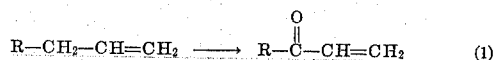
The present invention concerns multifunctional additives for oil compositions including gasolines, fuel oils, heating oils, and lubricating oils. The invention is also directed to the preparation of these additives and to oil compositions containing them. The additives can be characterized as oil-soluble imine or Schiff base derivatives of high molecular weight unsaturated ketones.

Numerous addition agents are known in the prior art for improving the desirable properties of fuels and lubricants, including high oxidation resistance, freedom from the formation of insoluble material, protection from rust and corrosion, and the like. For heavy duty service in high compression internal combustion engines, it is required that the lubricants contain additives that will impart good dispersancy and detergency as well as good oxidation stability. By dispersancy is meant the prevention of the deposition of insoluble material and by detergency is meant the quality of removing deposits where they have been formed. Recent emphasis in this field of additives has been placed on development of metal-free additives that will not form an ash. The conventional metal-containing additives have the disadvantage of leaving an ash residue which tends to accumulate in the combustion chamber of the engine and cause spark plug fouling, valve burning, preignition, and similar undesirable conditions. Ash-free dispersants are also of advantage in diesel fuels, fuel oil compositions, and gasolines as well. Additives that will function not only as good dispersants and detergents but that will additionally furnish protection from wear and from rust and corrosion are of particular value.

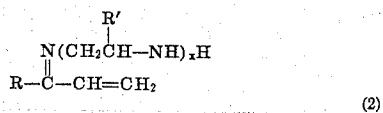
DESCRIPTION OF THE INVENTION

It has now been found in accordance with the present invention that highly effective dispersants and inhibitors for lubricating oils and fuels can be prepared by the mild oxidation of long chain terminal olefins to form unsaturated ketones which are then reacted with aliphatic polyamines to form imines or Schiff bases.

The oxidation of the olefin to an unsaturated ketone can be represented by the following equation:



In the above formula, R represents the remainder of the starting olefin. When this vinyl alkyl ketone is condensed with an aliphatic polyamine, an imine is formed which may be represented by the following formula:



In the above formula, R has the same meaning as in the previous formula, R' is selected from the group consisting of hydrogen and C₁ to C₃ alkyl groups, and x is a number from 1 to 10.

The starting materials for the preparation of the unsaturated ketones are aliphatic terminal olefins having from about 12 to about 250 carbon atoms, and preferably from about 16 to about 180 carbon atoms. Such olefins can be obtained from a number of sources, most commonly by the cracking of paraffin wax or by the polymerization or copolymerization of C₂ to C₅ mono-olefins, e.g., ethylene, propylene, butylene, isobutylene, or pentene. These long chain olefins can be straight chain or branched chain, but they must be terminal olefins, i.e., those containing a =CH₂ group. Representative olefin polymers that can be oxidized include a propylene polymer averaging about 36 carbon atoms per molecule, an ethylene polymer of about 2,000 molecular weight, a copolymer of about 70 weight percent ethylene and about 30 weight percent propylene of about 3,000 number average molecular weight, and a polyisobutylene of about 1,800 molecular weight. Ethylene-propylene copolymers of molecular weights within the range used in this invention are described in British Pat. No. 993,744. Low molecular weight polymers of aliphatic alpha olefins of 10 to 28 carbon atoms can also be oxidized for use in this invention. See U.S. Pat. No. 3,252,771. Polymers of C₂ to C₅ mono-olefins, and especially of isobutylene, of average molecular weights within the range of about 400 and 2,500 are particularly useful.

It is evident that in most instances the ketones will be mixtures of ketones of a range of molecular weights.

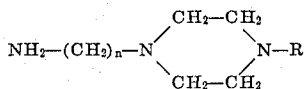
The oxidation of the olefin to form a vinyl alkyl ketone is most conveniently effected by the use of air or other oxygen-containing gas mixtures in the presence of a suitable catalyst. The latter include oxides of manganese, selenium, and chromium as well as C₁ to C₅ aliphatic acid salts of such metals, such as manganese acetate. Oxidation by air blowing can be conducted at temperatures ranging from about 150°F. to about 480°F. for from about 2 to 48 hours in the presence of from about 0.2 to about 10 wt. percent of catalyst; preferably at 250°F. to about 350°F. for from about 6 to 24 hours in the presence of from about 0.5 to 5 wt. percent of catalyst. Catalyst may be removed from the product very readily by filtration.

The ketone obtained by the oxidation of the olefin is converted to a Schiff base derivative by reacting the ketone with an alkylene polyamine. Generally, the mole ratio of polyamine to ketone will range from about 0.2 to 1 to about 1.5 to 1, although it is preferred that this ratio be in the range from about 0.5 mole of polyamine per ketone up to about 1.0 mole of polyamine per ketone. The reaction temperature will generally be in the range from about 140°F. to about 350°F. In most cases, however, a narrower range of from about 180°F. to about 250°F. will be used. The reaction time will depend to some extent on the reaction temperature. The composition of the reaction mixture can be determined by measuring the amount of water that is split off during the reaction. It is usually advantageous to employ a water-entraining solvent such as heptane, benzene, or toluene to remove the water as an azeotrope. Reaction will require from 1 to 48 hours, but will usually be complete in from about 2 to 12 hours.

The aliphatic polyamine that is employed in preparing the reaction products of the present invention can be an alkylene polyamine fitting the following general formula:

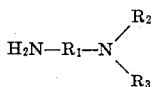


wherein n is 2 to 4 and m is a number from 0 to 10. Specific compounds coming within the formula include diethylene triamine, triethylene tetramine, tetraethylene pentamine, dibutylene triamine, dipropylene triamine, octaethylene nonamine, and tetrapropylene pentamine. N,N-di-(2-aminoethyl) ethylene diamine can also be used. Other aliphatic polyamine compounds that can be used include the N-aminoalkyl piperazines of the formula:



wherein n is a number 1 to 3, and R is hydrogen or an aminoalkyl radical containing 1 to 3 carbon atoms. Specific examples include N-(2-aminoethyl) piperazine, N-(2-aminoisopropyl) piperazine, and N,N'-di-(2-aminoethyl) piperazine.

Still other alkylene amino compounds that can be used include dialkylamino alkyl amines such as dimethylamino methyl amine, dimethylamino propyl amine, methylpropylamino amyl amine, etc. These may be characterized by the formula:

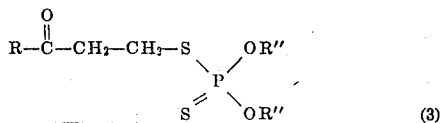


wherein R_1 is an alkylene radical, e.g., an ethylene, propylene, or butylene radical, and R_2 and R_3 are C_1 to C_3 alkyl radicals.

Thus, the alkylene polyamine or aliphatic polyamine compounds used in this invention can be broadly characterized as alkylene amino compounds containing two to 12 nitrogen atoms wherein pairs of nitrogen atoms are joined by alkylene groups of from two to four carbon atoms.

The use of mixtures of alkylene polyamines, dialkylamino alkyl amines, mixtures of N-aminoalkyl piperazines, and mixtures of the alkylene polyamines with the N-aminoalkyl piperazines is also contemplated.

The Schiff base derivatives of the present invention may be modified to impart antiwear and antirust properties by incorporating therein phosphorus thioacid groups. One method of accomplishing this is to form an addition compound between the unsaturated ketone and a dihydrocarbyl dithiophosphoric acid. Preferably, the ketone is reacted with the dithiophosphoric acid prior to the step of forming the imine. More or less equal molar proportions of the two reactants are reacted at a temperature in the range of from about 60°F. to about 300°F. or more particularly from about 100°F. to about 200°F. The reaction time may take from 4 to 30 hours, depending somewhat on the reaction temperature and it may be promoted with a catalyst such as tert. butyl perbenzoate. It is believed that the adduct that is formed results from attachment of the acidic sulfur atom of the dithiophosphoric acid to the double bond of the unsaturated ketone, giving a compound of the following formula:



In the above formula R has the same meaning as in the previous formulas and R'' is the hydrocarbon group of the dihydrocarbon dithiophosphoric acid that is used in preparing the adduct. R'' may be the same or different hydrocarbon radicals including aryl, alkyl, aralkyl, and cycloalkyl radicals. These radicals may have from one to 20 carbon atoms, and preferably have from one to 12 carbon atoms each. Examples of suitable dihydrocarbyl dithiophosphoric acids include diisobutyl dithiophosphoric acid, lauryl phenol dithiophosphoric acid, mixed ethyl isopropyl dithiophosphoric acid, ditertiary octyl dithiophosphoric acid, mixed isopropyl C_n oxo dithiophosphoric acid, dilauryl dithiophosphoric acid, mixed isobutyl primary amyl dithiophosphoric acid, diphenyl dithiophosphoric acid, mixed dithiophosphoric acids derived from mixed alcohols from paraffin wax oxidation, mixed hexyl stearyl dithiophosphate, mixed isopropyl C_{13} oxo dithiophosphoric acid and mixed dithiophosphates derived from mixed C_{10} to C_{18} alcohols known as "Lorol" alcohols and so forth.

The phosphorus thioacid function can also be introduced into the ketone by treatment of the unsaturated ketone with a sulfide of phosphorus, preferably with P_2S_5 . The ketone may be reacted with from about 5 to about 40 wt. percent of the phosphorus sulfide and is preferably treated with from about 10 to 30 wt. percent of the sulfide of phosphorus. Reaction temperatures will be in the range of from about 100°F. to about 260°F. or more preferably from about 160°F. to about 230°F. with reaction times of from 0.5 to 10 hours or more usually of from about 1 to 6 hours.

The nature of this invention will be further understood when reference is made to the following examples, which include preferred embodiments.

EXAMPLE 1

The starting material for this preparation was a cut of higher olefins containing from 20 to 28 carbon atoms. The cut contained 90 wt. percent alpha-olefins, 6 percent of other olefins, and 4 percent of saturated hydrocarbons, and predominated in C_{20} hydrocarbons (93%). It had a specific gravity of 0.798 at 68°F. A suspension of 10 grams of manganese dioxide in 500 grams of the olefins was prepared and was subjected to constant agitation. Air was passed through the agitated suspension for 24 hours at 330°F. At the end of this time the mixture was filtered to remove the manganese dioxide. The yield of product was 450 grams. Strong carbonyl bands at 5.85 millimicrons were found upon infrared analysis, indicating that ketones had been formed.

The product of oxidation was converted to an imine by mixing 90 grams of the above ketone product with 10 grams of tetraethylene pentamine and 100 grams of heptane and heating the resulting mixture under reflux for 6 hours, during which time 1 gram of water was collected in the reflux trap. The reaction product was filtered and then stripped of heptane. A dark brown viscous product was obtained in a yield of 85 grams.

EXAMPLE 2

A mixture was prepared consisting of 10 grams of manganese dioxide and 400 grams of polyisobutylene

of 960 avg. mol. wt. The mixture was stirred for 24 hours at 355° - 360°F. while air bubbles were passed through the mixture. At the end of this time, the mixture was filtered to remove the manganese dioxide catalyst. The product had an oxygen content of 4.6 wt. percent and infrared analysis showed a strong band at 5.75 millimicrons, indicating the presence of ketones.

The product of oxidation was converted to an imine by mixing 25 grams of the oxidized material with 25 grams of a solvent neutral lubricating oil of 150 SUS viscosity at 100°F. and 1.25 grams of tetraethylene pentamine and heating the mixture at 250°F. (120°C.) for 8 hours. The reaction product had a nitrogen content of 0.88 wt. percent.

EXAMPLE 3

The oxidation step of Example 2 was repeated, again using 400 grams of 960 mol. wt. polyisobutylene and 10 grams of manganese dioxide. The reaction time was 24 hours and the reaction temperature was about 390° - 395°F. (200°C.).

In the same manner as in Example 2, the product of oxidation was converted to an imine or Schiff base, but in this case using different proportions of the ketone product and tetraethylene pentamine. In each case 25 grams of the oxidation product and 25 grams of a solvent neutral lubricating oil were used, but the amounts of tetraethylene pentamine were 1 gram, 0.5 gram, and 0.3 gram, respectively. The reaction time in each case was 8 hours and the reaction temperature was about 200°F. (120°C.). The products are hereinafter referred to, in order of decreasing amounts of tetraethylene pentamine, as Products 3A, 3B and 3C, respectively.

EXAMPLE 4

A cut of C₁₈ olefins obtained by the cracking of paraffin wax was air oxidized in the manner described in Example 1. The olefin cut contained 80 wt. % alpha-olefins and 5 to 6 wt. percent of aromatic hydrocarbons. Branched chain aliphatic hydrocarbons were present in the equivalent of 1.3 methyl groups per molecule. A 100-gram portion of the air-oxidized product was reacted with 24 grams of P₂S₅ at 212°F. The P₂S₅ was added gradually over a period of 3 hours. The P₂S₅ treated product was mixed with 100 grams of heptane and with 15 grams of tetraethylene pentamine. The mixture was heated under reflux for 12 hours, after which time the reaction product was filtered and then stripped of heptane. The yield of product was 120 grams.

EXAMPLE 5

For this preparation mixed dialkyl dithiophosphoric acids were employed which were obtained by treating a mixture of isobutanol and mixed amyl alcohols with P₂S₅. A mixture was prepared consisting of 43 grams of the mixed dialkyl dithiophosphoric acids, 300 grams of the unsaturated ketone product from C₂₀ to C₂₈ olefin oxidation used in Example 1, 200 grams of heptane and 4 grams of tertiary butyl perbenzoate. This mixture was heated at 185°F. for 20 hours under an atmosphere of nitrogen. Then 30 grams of tetraethylene pentamine were added and the mixture was heated under reflux at 230°F. Four milliliters of water were collected at the end of the reaction. The heptane was then stripped from the product. The solvent-free material was ob-

tained in a yield of 350 grams and was found on analysis to have a nitrogen content of 2.62 wt. %.

EXAMPLE 6

To one portion of a lubricating oil base stock of SAE 30 viscosity rating there was added by simple mixing 1 wt. percent of the product of Example 5. To another portion of the same base oil there was added 1 wt. percent of a zinc dialkyl dithiophosphate concentrate, which was an oil solution consisting of about 25 wt. percent mineral lubricating oil and about 75 wt. percent of zinc dialkyl dithiophosphates prepared by zinc oxide neutralization of the mixed dialkyl dithiophosphoric acids employed in Example 5.

These two compositions were subjected to the Falex wear test, which involves running the test compositions in a Falex wear testing machine for 30 minutes at 500 pounds direct gauge reading. The results obtained are given in the following Table I.

TABLE I

Additive	Falex wear, mg.
Product of Example 5	2.0
Zinc dialkyl dithiophosphate	5.6

It will be seen from Table I that the additive of Example 5 was superior to a conventional zinc dialkyl dithiophosphate with respect to wear reduction.

EXAMPLE 7

The additive concentrates obtained as described in Example 2 and 3 were mixed with separate portions of a used lubricating oil (described below) in 0.5 wt. percent concentration, thus effecting the incorporation of about 0.25 wt. percent of actual additive. Another blend was prepared by adding to another portion of the same oil about 0.5 wt. percent of a commercial dispersant concentrate, the dispersant being the imide obtained by condensing 2.8 moles of polyisobutenyl succinic anhydride with one mole of tetraethylene pentamine. The polyisobutenyl succinic anhydride was derived from about 1,000 average molecular weight polyisobutylene. The commercial additive concentrate contained about 50 wt. percent active ingredient, thus the used oil blend contained 0.25 wt. percent of actual dispersant additive.

All of the used oil blends thus prepared were subjected to a sludge dispersancy bench test which had been found, after a large number of evaluations, to be an excellent screening test for lubricating oil dispersant additives.

The sludge dispersancy bench test was conducted in the following manner. The medium chosen for the sludge test was a used oil (original viscosity about 325 SUS at 100°F.) that had been run in a fleet of taxicabs in New York City. This used oil contained a fine dispersion of actual engine sludge. About 10 ml. of each of the blends described above, i.e., blends of the test additives in the used oil described, was placed in a centrifuge tube and then centrifuged in a conventional centrifuge for one hour at 3,600 rpm. It was observed that after this period of time a sludge-free region with a closely defined boundary formed at the top of the centrifuge tube. The relative length of this sludge-free region with respect to the total length of the sample in the centrifuge tube was determined. The lower the per-

centage of oil separation, the better the additive is as a dispersant. The used oil alone gave greater than 90 percent separation into a clear oil layer. The various blends of used oil and additive gave the results shown in Table II, which follows:

TABLE II

Additive	Sludge Dispersancy Bench Test % Clear Oil
Product of Example 2	48
Product 3A	41
Product 3B	35
Product 3C	46
Commercial Dispersant	49

It is seen from the data that the products were at least equally as effective as the imide dispersant of the prior art as dispersing agents for sludge in a crankcase lubricant.

EXAMPLE 8

Using as the base oil a mineral lubricating oil having a viscosity of 325 SUS at 100°F. and a viscosity index of about 100, a reference blend was prepared by simple mixing of 3.5 wt. percent of a commercial detergent inhibitor, 0.9 wt. percent of a zinc dialkyl dithiophosphate antiwear additive and 95.6 wt. percent of the base oil.

Test compositions were prepared by simple mixing of 3.5 wt. percent of the same detergent inhibitor, 0.9 wt. percent of the same antiwear additive and 93.6 wt. percent of the same base oil as in the reference blend along with 1 wt. percent of the product of Example 1.

The commercial detergent inhibitor mentioned above was a mineral oil solution containing an additive prepared by reacting a mixture of a phosphosulfurized polyisobutylene and nonyl phenol with barium hydroxide pentahydrate and blowing the reaction mixture with carbon dioxide. The approximate analysis of the concentrate was 27 wt. percent of phosphosulfurized polyisobutylene, 11.7 wt. percent nonyl phenol, 10.6 wt. percent barium oxide, 2.5 wt. percent carbon dioxide, and 48.2 wt. percent of mineral oil.

The zinc dialkyl dithiophosphate antiwear additive was an oil solution consisting of about 25 wt. percent of mineral lubricating oil and about 75 wt. percent of zinc dialkyl dithiophosphate prepared by treating a mixture of isobutanol and mixed amyl alcohols with P_2S_5 followed by neutralizing with zinc oxide.

Each of the compositions was tested for sludge dispersing ability in a Cyclic Temperature Sludge Test which, from prior experience, has been shown to give sludge deposits similar to those obtained in stop-and-go driving such as would be experienced in taxicab operation. Briefly described, in this test a Ford 6-cylinder engine is run on a dynamometer stand through alternate cycles, the first cycle lasting 5 hours, at 1,500 rpm, and the second cycle lasting 2 hours, at the same operating speed, with the oil sump and water jacket temperatures being slightly higher in the second cycle than in the first. The two cycles are alternated in sequence until the desired total test time has elapsed. Make-up oil is added as required so as to maintain the oil level in the crankcase at all times between about 3-1/2 and 4 quarts. At the end of selected periods of test time, the engine is inspected by disassembling it sufficiently to permit visual examination of several of the parts, including the

rocker arm assembly, the rocker arm cover, the cylinder head, the push rod chamber and its cover, the crankshaft and the oil pan. These parts are visually and quantitatively rated for sludge deposits using a CRC Sludge Merit rating system in which a numerical rating of 10 represents a perfectly clean part, and the numerical scale decreases to a minimum value representing a part covered with the maximum amount of sludge possible. The several merit ratings are averaged to give an overall engine merit rating.

The results of the cyclic temperature sludge test are summarized in Table III. It will be seen from these results that the additive product of Example 1 greatly increased the ability of the oil composition to disperse sludge.

TABLE III

Test Hours	Sludge Merit Ratings — Cyclic Temperature Test	
	Reference Blend	Reference Blend Plus Additive of Example 1
42	8.6	—
63	6.9	9.63
84	5.8	9.20
105		8.0

The additives of this invention may be employed in concentrations ranging from about 0.002 to about 10 wt. percent in oil compositions ranging from gasoline fractions through middle distillate fuels and lubricating oils.

For use as lubricating oil additives the reaction products of this invention may be incorporated in lubricating oil compositions in concentration ranges of from about 0.1 to about 10 wt. percent on an actual ingredient basis, and will ordinarily be used in concentrations of from about 0.1 to about 5 wt. percent. The lubricating oils to which the additives of the invention may be added include not only mineral lubricating oils, but synthetic oils also. The mineral lubricating oils may be of any preferred types, including those derived from the ordinary paraffinic, naphthenic, asphaltic, or mixed base mineral crude oils by suitable refining methods. Synthetic hydrocarbon lubricating oils may also be employed. Other synthetic oils include dibasic acid esters such as di-2-ethyl hexyl sebacate, carbonate esters, phosphate esters, halogenated hydrocarbons, polysilicones, polyglycols, glycol esters such as C_{13} oxo acid diesters of tetraethylene glycol, and complex esters as for example the complex ester formed by the reaction of 1 mole of sebacic acid with 2 moles of tetraethylene glycol and 2 moles of 2-ethyl hexanoic acid.

The additives of this invention may also be employed in middle distillate fuels for inhibiting corrosion and the formation of sludge and sediment in such fuels. Concentration ranges of from about 0.002 to about 2 wt. percent, or more generally, from about 0.005 to about 0.2 wt. % are employed. Petroleum distillate fuels boiling in the range of from about 300°F. to about 900°F. are contemplated. Typical of such fuels are No. 1 and No. 2 fuel oils that meet ASTM Specification D-396-48T, diesel fuels qualifying as Grades 1D, 2D and 4D of ASTM Specification D-975-51T, and various jet engine fuels. Because they are ashless, these additives are particularly desirable for such fuels in that they do not give rise to glowing ashes nor deter from the burning qualities of the distillates. Thus, for instance, about 0.04 wt. percent of the product of Example 1 can be

added to a heating oil comprising a mixture of cracked and straight run distillates having a boiling range of about 350° to 680°F. These additives may also be used in conjunction with other prior art ashless additives for fuels, such as polymers of acrylic or methacrylic acid esters, high molecular weight aliphatic amines, etc.

The additives of this invention may also be employed either alone or in combination with other hydrocarbon-soluble additives, in jet fuels and gasolines in concentrations ranging from about 0.001 to 1.0 wt. percent as detergent and/or rust preventive additives. Thus, about 0.007 wt. percent of the concentrate of Example 2 can be added to a leaded gasoline to impart carburetor detergency action thereto. The gasoline contains 3 cc. of lead tetraethyl per gallon and has an initial boiling point of 85°F., a 50 percent point of 205°F. and a final boiling point of 380°F.

In either the fuel or lubricant compositions, other conventional additives may also be present, including dyes, pour-point depressants, antiwear agents, e.g., tricresyl phosphate, zinc dialkyl dithiophosphates of three to eight carbon atoms, antioxidants such as phenyl-alpha-naphthylamine, tert. octylphenol sulfide, bisphenols such as 4,4'-methylene bis (2,6-di tert. butylphenol), viscosity index improvers such as polymethacrylates, polyisobutylene, alkyl fumarate-vinyl acetate copolymers, and the like, as well as other dispersants. Thus, a compounded lubricant suitable for use as a crankcase oil can be prepared by blending into a light mineral lubricating oil base stock sufficient viscosity index improver (e.g., 15,000 molecular weight polyisobutylene) to place it in the SAE 10W-30 viscosity class along with 0.8 wt. percent of a high alkalinity calcium synthetic alkyl aromatic sulfonate of 11.4 wt. percent calcium content and 300 total base number, 0.5 wt. percent of a pour point depressant (wax-alkylated naphthalene) and 1.8 wt. percent of the product of Example 1.

The dispersant additives of the invention may be employed to enhance the dispersancy-detergency of lubricants containing conventional detergents, wherein the latter are used in concentrations in the range of about 0.5 to 5 wt. percent. When the conventional detergents or dispersants are metal-containing materials it is possible, by utilizing the additives of the present invention in combination therewith, to obtain added dispersancy or detergency without materially increasing the total ash-forming properties of the composition. Such metal-containing detergents or combination detergent inhibitors include the alkaline earth metal salts of alkylated phenols or of alkylated phenol sulfides, as for example barium-calcium nonyl phenol sulfide, the so-called basic alkaline earth metal sulfonates, and dispersions of barium carbonate or calcium carbonate in mineral oils containing various surfactants such as phosphosulfurized polyolefins, for example. Specific examples of suitable sulfonates include calcium petroleum sulfonate, barium petroleum sulfonate, calcium di-C₉ alkyl benzene sulfonate (C₉ group from tripropylene) and barium C₁₆ alkyl benzene sulfonate (C₁₆ group from tetraisobutylene). The sulfonates may be of either the neutral type or of the "over-based" or "high alkalinity" type. Metal salts of alkyl phenols and of the corresponding alkyl phenol sulfides that are ordinarily employed as detergents are those derived from phenols having alkyl groups of from five to 20 carbon atoms. Specific examples are barium tert. octyl phenol sulfide,

and the barium salt of the alkylation product of phenol with tripropylene.

Other detergent additives include the reaction products of phosphosulfurized hydrocarbons with alkaline earth metal oxides or hydroxides which can be prepared by first treating a hydrocarbon with a phosphorus sulfide and then reacting the product with an alkaline earth metal hydroxide or oxide, for example barium hydroxide, preferably in the presence of an alkyl phenol or an alkyl phenol sulfide and also preferably in the presence of carbon dioxide.

The dispersants of this invention may also be used in conjunction with other ashless detergents or dispersants such as high molecular weight polymeric dispersants made with one or more polar monomers, such as vinyl acetate, vinyl pyrrolidone, methacrylates, fumarates and maleates. These dispersants have molecular weights in the range of about 500 to 50,000. One example is a copolymer of 65 to 85 wt. percent of mixed C₉ to C₁₂ fumarates, 10 to 20 wt. percent of vinyl acetate, and 5 to 15 wt. percent of N-vinyl pyrrolidone.

It is within the contemplation of this invention to prepare additive concentrates in which the concentration of additive is greater than would normally be employed in a finished lubricant. These concentrates may contain in the range of from 10 to 80 percent of additive on an active ingredient basis, the balance being a hydrocarbon oil, usually a mineral oil. Such concentrates are convenient for handling the additive in the ultimate blending operation into a finished lubricating oil composition. The additive concentrates may be made up simply of an additive of the present invention in a suitable mineral oil medium or they may include other additives that are intended for use along with the additives of the invention in a finished lubricant.

While the lubricant compositions herein described are primarily designed as internal combustion engine crankcase lubricants, the additives of the invention may also be employed in other oil compositions, including turbine oils, various industrial oils, gear oils, hydraulic fluids, transmission fluids and the like.

It is to be noted that in the present invention the existence of the double bond in the vinyl alkyl ketone provides an additional site for reaction with amino groups as compared with a saturated ketone, thus incorporating additional amino groups into the additive and thereby imparting greater dispersancy. Furthermore, in this Michaels addition type of reaction at the double bond, both primary and secondary amino groups can be reacted, whereas only primary amino groups can react with the keto groups. Thus, with a vinyl alkyl ketone there is much more opportunity for reaction with aliphatic polyamines than when using saturated ketones.

What is claimed is:

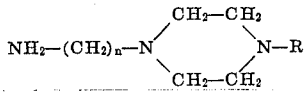
1. A Schiff base soluble in an oil selected from the class consisting of gasoline, middle distillate petroleum fuels and lubricating oils, and imparting dispersant properties to said oil which comprises the product obtained by reacting, at a temperature of from about 140°F. to about 350°F., and for a time sufficient to split out water and effect the necessary reaction, from 0.2 to 1.5 moles of an aliphatic polyamine with one mole of an alkyl vinyl ketone having from 16 to about 180 carbon atoms that has been obtained by the mild oxidation of a terminal olefin of the same number of carbon atoms, said aliphatic polyamine being selected from the

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class consisting of N,N-di-(2-aminoethyl) ethylene diamine, alkylene polyamines having the formula:



wherein n is 2 to 3 and m is a number from 0 to 10, and N-aminoalkyl piperazines of the formula:



wherein n is a number 1 to 3 and R is selected from the group consisting of hydrogen and aminoalkyl radicals of 1 to 3 carbon atoms.

2. An oil-soluble Schiff base as defined by claim 1

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wherein said ketone is a mixture of ketones derived from a polymer of a C₂ to C₅ monoolefin.

3. An oil-soluble Schiff base as defined by claim 1 wherein said ketone is a mixture of ketones derived by the oxidation of polyisobutylene of average molecular weight within the range of about 400 to 2,500.

4. An oil-soluble Schiff base as defined by claim 1 wherein said ketone is a mixture of ketones derived from the olefins of cracked paraffin wax.

5. An oil-soluble Schiff base as defined by claim 1 wherein said ketone is a mixture of ketones of from 20 to 28 carbon atoms.

6. An oil-soluble Schiff base as defined by claim 1 wherein said aliphatic polyamine is tetraethylene pentamine.

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