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ARYL KETO ACID POUR-POINT DEPRESSANTS AND DISPERSANTS FOR OLEAGINOUS COMPOSITIONS

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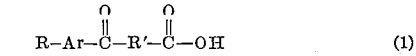
This invention concerns improved oil-soluble ester additives that are capable of serving multiple functions in oleaginous compositions of the class of gasolines, fuel oils, heating oils and lubricating oils. These additives may be characterized as esters of alkaryl keto carboxylic acids and polyhydroxy organic compounds. The invention is also directed to the preparation of these additives and to oleaginous compositions containing them.

The satisfactory lubrication of modern high compression engines requires the use of a heavy duty type of lubricating oil containing detergent additives that will impart good detergency, efficient sludge dispersion action and high oxidation resistance. In recent times, it has been recognized that additives of this nature that are relatively free of metal content are preferred to the conventional metal-containing additives because the latter materials leave an ash residue which tends to accumulate in the combustion chamber of the engine and there cause pre-ignition, valve burning, spark plug fouling, and similar undesirable conditions. For this reason, an effective dispersant that is ash-free is preferable to an ash-forming detergent additive such as an alkaline earth metal sulfonate, a metal salt of an alkylated phenol or the like.

To satisfy all of the requirements of a modern internal combustion engine lubricant, it is also necessary to incorporate other additives which will lower the pour point of the oil, increase its oxidation resistance, raise its viscosity index and the like. An additive that will provide several of these functions is highly desirable.

It has now been found, in accordance with the present invention, that effective ash-free mineral-oil-soluble detergent inhibitors and dispersants that also possess pour point depressant properties can be prepared by condensing polyhydric organic compounds with certain alkylated aryl keto carboxylic acids derived from alkylated aryl compounds.

The keto acids that are employed in this invention may be characterized by the following general formula:



(1)

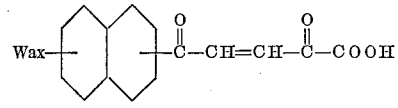
In the above formula R is at least one aliphatic hydrocarbon radical having in the range of from 12 to 30 carbon atoms and R′ is a hydrocarbon radical having in the range of from 2 to about 18 carbon atoms, preferably from about 2 to 6 carbon atoms. The symbol Ar in the above formula is an aromatic radical having in the range of 6 to 16 carbon atoms which may be a cyclic hydrocarbon, a short-chain-alkylated cyclic hydrocarbon, or a hydroxy derivative of either, such as phenol, a C_1 to C_6 alkyl phenol, naphthol, benzene, toluene, xylene, other C_1 to C_6 alkyl benzenes, naphthalene, anthracene or phenanthrene. Preferably it is derived from naphthalene. The symbol R in the above formula is preferably derived from paraffin wax hydrocarbons, i.e., by alkylating naphthalene, benzene, phenol, or the like with halogenated paraffin wax, although the alkylation may be effected with other halogenated paraffin hydrocarbons in the C_{12} to C_{30} range, e.g., chlorinated dodecane, brominated cetane, chlorinated gas oil, chlorinated kerosene, etc.

The keto acids are prepared by condensing the alkylated aryl compounds of the above-mentioned types with a dibasic acid or its anhydride or with a dibasic acyl halide

in the presence of a Friedel-Crafts catalyst, such dibasic acid compounds having a total carbon content of from 4 to 20 carbon atoms, and more preferably from 4 to 8 carbon atoms.

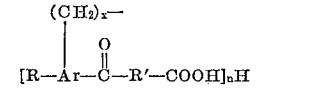
Especially preferred for use in this invention are the keto acids derived by condensing alkyl aromatics, and particularly wax alkylated naphthalene, with succinic acid or with maleic acid or their anhydrides, in which case R′ will be —CH_2—CH_2— or CH=CH, respectively. Other dibasic acids or their anhydrides that may be used include citraconic acid, itaconic acid, glutaric acid, suberic acid and adipic acid. A related keto acid that may be employed is that derived by condensing wax alkylated naphthalene or other alkylated aryl compounds of the types disclosed with phthalic anhydride, in which case R′ will be a cyclic C_6 radical. Other keto acids can be prepared by condensing the alkylated aryl compounds with dibasic acyl halides such as the acid chlorides or mixed-acid acid chlorides of suberic acid, sebacic acid, adipic acid or azelaic acid.

The keto acid prepared from wax alkylated naphthalene and maleic anhydride could have the formula:



(2)

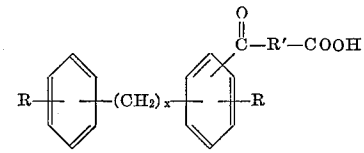
In the alkylation of the aromatic compounds with halogenated aliphatic hydrocarbons, such as chlorinated paraffin wax, it is possible to have two or more aromatic nuclei joined by aliphatic hydrocarbon linkages, so that the keto acids derived from the alkylated aromatics could have a formula of the following nature:



(3)

wherein R is hydrogen or an aliphatic radical of from 12 to 30 carbon atoms, R′ is a hydrocarbon radical having in the range of from 2 to about 18 carbon atoms, Ar is the aromatic nucleus, x is a number from 12 to 30, and n is a number from 1 to 10.

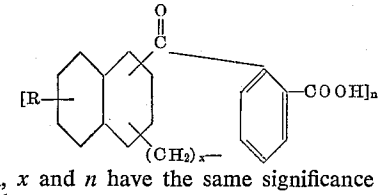
It is also possible to have a structure wherein not all of the aryl groups have keto acid substituents, as for example:



(4)

R, R′, and x having the same significance as in Formula 3.

It is believed that the keto acid prepared by condensing wax alkylated naphthalene with phthalic anhydride has the structure:



(5)

where R, x and n have the same significance as in Formula 3 above.

The alkylation of the aromatic compounds for the purpose of preparing alkaryl keto acids for use in this invention may be conducted by any of the means known to the art. The most common alkylation procedure involves alkylation with either an olefinic hydrocarbon, e.g., a propylene polymer or an isobutylene polymer, or an alkyl halide, such as cetyl bromide, aided by a Friedel-Crafts catalyst, normally either $AlCl_3$ or BF_3.

The preparation of alkylated naphthalenes by the Friedel-Crafts condensation of halogenated aliphatic hydrocarbons with naphthalene is well known and is disclosed, for example, in U.S. Patents 1,815,022 and 2,015,-748. Briefly, the reaction involves the halogenation (preferably chlorination) of an aliphatic hydrocarbon of from about 12 to about 30 carbon atoms until the product contains about 10 to 15 weight percent of chlorine. The halogenated material is then condensed with naphthalene in the presence of aluminum chloride or similar Friedel-Crafts catalysts. For example, paraffin wax or petrolatum may be chlorinated at a temperature in the range of 140° to 300° F. until it contains 10 to 14% chlorine and it may then be condensed with naphthalene at 140° to 160° F. with the acid of a Friedel-Crafts catalyst. As a specific example, 9 parts of chlorinated wax can be condensed with one part of naphthalene, using as a catalyst 1 part by weight of aluminum chloride.

To prepare the alkaryl keto acids for use in this invention, the wax alkylated naphthalene or similar alkylated aromatic hydrocarbon or alkylated phenol is condensed with an acid anhydride or with an acid chloride as hereinbefore described in the presence of a Friedel-Crafts catalyst, such as $AlCl_3$, BF_3, or the like. In the case of the condensation of wax alkylated naphthalene with maleic anhydride or with succinic anhydride, the reactants are employed preferably in equimolar proportions, although some excess, e.g., up to 100% excess of the acid anhydride, may be used in the reaction. The condensation may be effected at temperatures ranging from room temperature to about 250° F., the preferred range being from about 100° F. to about 150° F. Reaction times may range from 1 to 12 hours and will usually require 3 to 8 hours. The mole proportion of Friedel-Crafts catalyst to acid anhydride may range from about 0.5 to 1 to about 2 to 1. It will generally range from about 0.5 to 1 to about 1.25 to 1.

For convenience in handling, it is preferred to dissolve the reactants in a suitable solvent such as orthodichloro benzene, cyclohexane, normal heptane, or similar solvents having no tertiary hydrogen atoms. After the reaction has been completed, the resulting keto acid is washed with a dilute mineral acid such as dilute hydrochloric acid, and then with water to remove the Friedel-Crafts catalyst.

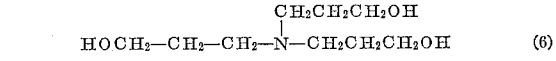
It is possible to conduct the steps of alkylating the aromatic hydrocarbon or related hydroxy derivative and the step of converting the alkylated material to the keto acid in one operation, i.e., by reacting the aromatic hydrocarbon or the like with the alkylating agent, e.g., chlorinated wax or an alkyl halide, and with the acrylating agent, e.g., the acid anhydride or acid halide, in the presence of a Friedel-Crafts catalyst, e.g., $AlCl_3$.

To prepare the additives of the present invention, the above-described keto acids are condensed with aliphatic polyhydroxy compounds from the class consisting of polyhydric alcohols having from 2 to 10 carbon atoms and from 2 to 6 hydroxy groups, polyalkylene glycols of from 100 to 600 molecular weight, and polyhydroxy alkyl amines having from 5 to about 30 carbon atoms, from 2 to 6 hydroxy groups, and from 1 to 4 tertiary amino groups.

The polyhydric alcohols include glycols, trihydric alcohols, tetrahydric and pentahydric alcohols and the hexitols, such as: ethylene glycol; 1,3-propanediol; pinacol; 1,5-pentanediol; neopentyl glycol; decamethylene glycol; glycerol; erythritol; mannitol; sorbitol; 2-ethyl-2-butyl-1,3-propanediol; 1,4,5-hexanetriol; dulcitol; 1,2,3-pentanetriol; and dimethylpentaneglycerol. The monoaldehyde and monoketo derivatives of the tri-, tetra-, penta-, and hexahydric alcohols may also be used, including erythrose, methyltetrose, arabinose, glycerose, glucose, xylose, fructose, and the like.

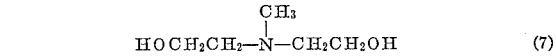
The polyalkylene glycols include diethylene glycol, triethylene glycol, dipropylene glycol, hexaethylene glycol, decaethylene glycol, mixed polyethylene glycols, etc.

The polyhydroxy alkyl amines used in this invention may be prepared by reaction of alkylene oxides with primary amines or with ammonia. Reaction of propylene oxide with ammonia can give a compound of the formula:



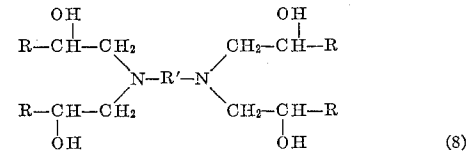
(6)

Methyl amine can be reacted with ethylene oxide to give a compound of the formula:



(7)

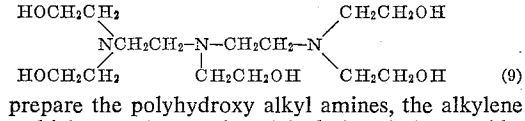
Particularly useful polyhydroxy alkyl tertiary amines are N,N,N',N' tetrakis (hydroxyalkyl) alkylene diamines, which may also be referred to as alkylene dinitrilotetraalkanols. These may be represented by the following general formula:



(8)

where R is a member selected from the group consisting of hydrogen atoms and alkyl groups containing 1 to 2 carbon atoms, and R' is an alkylene radical of from 2 to 6 carbon atoms. Some of the hydroxyalkyl alkylene diamines are available commercially. Specific examples of these compounds include ethylene dinitrilotetraethanol, propylene dinitrilotetrabutanol and ethylene dinitrilotetrapropanol.

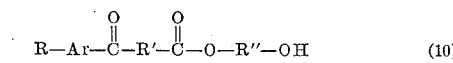
The above hydroxyalkyl alkylene diamines may be prepared by reacting an alkylene oxide containing 2 to 4 carbon atoms with an alkylene diamine such as ethylene diamine, propylene diamine, or hexamethylene diamine. In this reaction, about 4 moles of the alkylene oxide will be reacted with each mole of alkylene diamine. If the molar proportions are changed, other polyhydroxy alkyl amines useful in this invention are obtained, such as the following:



(9)

To prepare the polyhydroxy alkyl amines, the alkylene oxides which may be employed include ethylene oxide, propylene oxide, and butylene oxide. Mixtures of these alkylene oxides may be used if desired. The reaction between the alkylene oxide and the amine may be conveniently carried out at a temperature in the range of about room temperature to 500° F., generally about 200° F. to 400° F., and the reaction will be completed generally within about 4 to 6 hours, with or without the application of external pressure, e.g. 25 to 30 pounds per square inch.

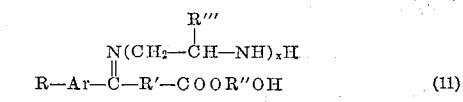
When the keto acid and the polyhydroxy compound are reacted in equimolar portions, it is believed that the product of the reaction is primarily a simple ester indicated by the following general formula:



(10)

In the above formula R, R', and Ar have the same significance as in Formula 1, and R''—OH represents the residue of the polyhydric compound.

It is also possible to react the product represented by Formula 10 with an aliphatic polyamine, under conditions that form an imine or Schiff base by reaction of the amino group with the keto group. The product may include a compound represented by the following formula:



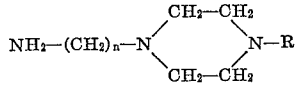
(11)

In the above formula R, R', and R' OH, and Ar have the same significance as in Formula 10, x is a number from 1 to 10 and R''' is selected from the group consisting of hydrogen and C_1 to C_3 alkyl groups.

For the Schiff base reaction, the temperatures will generally be in the range of from about 150° to about 280° F. preferably at 190 to 210° F. The reaction time will depend to some extent upon the reaction temperatures, generally at 2 hours to 48 hours, preferably at 8 hours to 10 hours. Preferably a water entraining agent such as heptane, benzene or toluene is employed to remove as an azeotrope the water that is split off during the reaction. In conducting the Schiff's base reaction the aliphatic polyamine that is employed may be an alkylene polyamine fitting the following general formula:

$$NH_2(CH_2)_n—NH(CH_2)_{n,m}—NH_2$$

wherein n is 2 to 3 and m is a number from 0 to 10. Specific compounds coming within the formula include diethylene triamine, tetraethylene pentamine, dipropylene triamine, octaethylene nonamine, and tetrapropylene pentamine. N,N-di-(2-aminoethyl) ethylene diamine may also be used. Other aliphatic polyamine compounds that may be used are the N-aminoalkyl piperazines of the formula:



wherein n is a number from 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.

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

As already stated, the additives of the present invention are esters of the alkaryl keto carboxylic acids and the polyhydroxy compounds above described. The esters are prepared from 1 mole of a selected polyhydroxy compound and 1 to 2 moles of keto acid. The esterification may be effected by any of the conventional techniques, the most general one being to heat a mixture of the reactants in the presence of a water-entraining agent such as heptane or toluene under reflux conditions and to trap water overhead. An acid catalyst such as p-toluene sulfonic acid may be necessary. Completion of the reaction, which may take from 2 to 24 hours or so, will be known when the calculated amount of water has been collected overhead. After the reaction is complete, the esters are recovered by stripping off the solvents, usually by distillation under vacuum.

It is believed that the formation of esters in accordance with the present invention enhances the dispersancy powers of the alkaryl keto acids by introducing polar groups. Since the polyalkylene glycols thereby introduce ether groups as well as hydroxyl groups, their use rather than the simpler polyhydric alcohols produces even more effective additives. The most effective additives are prepared by esterifying with the polyhydroxy alkyl amines because the latter add basicity to the additives as well as introducing additional polar groups.

The nature of this invention will be further understood when reference is made to the following examples:

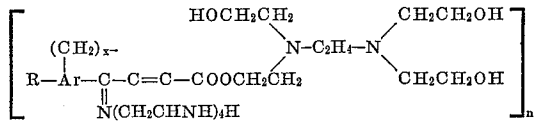
EXAMPLE 1

The starting material for the preparation of a keto acid was a 50 weight percent concentrate of a wax alkylated naphthalene in a solvent neutral mineral oil (viscosity 150 SUS at 100° F.). The wax alkylated naphthalene had been obtained by chlorinating a crude paraffin scale wax of 125° to 127° F. melting point to 14.5 weight percent chlorine content and condensing 200 grams of the

chlorinated wax with 25.6 grams of naphthalene with the aid of aluminum chloride catalyst.

A 400 gram portion of the wax alkylated naphthalene concentrate was mixed with 100 cc. of orthodichloro benzene. Then 32 grams of aluminum chloride and 20 grams of maleic anhydride were added and the mixture was heated in the range of 100° to 150° F. for about 4 hours. The product was then freed of aluminum chloride by washing it three times with 10 percent hydrochloric acid solution in an amount equal in volume to the product and then with water until it was found to be acid free. The orthodichloro benzene was then removed from the product by heating the latter to about 400° F. under reduced pressure (25 inches of Hg pressure). The active ingredient in the concentrate thus obtained was determined by infrared analysis to be a keto acid.

A 300 gram portion of the acid product concentrate obtained as above was mixed with 38 grams of ethylene dinitrilotetraethanol and 200 grams of toluene, and the mixture was heated under reflux, using as a catalyst 0.1 gram of paratoluene sulfonic acid. After the esterification reaction was completed as noted by the amount of water collected in the reflux water trap, 20 grams of tetraethylenepentamine were added to the ester product concentrate and refluxing was continued for an additional 8 hours. The final product after removal of the solvent by heating at 210° F. under reduced pressure (25 inches Hg) was an additive concentrate of approximately 50 weight percent oil and 50 weight percent additive. The nitrogen content of the concentrate was found on analysis to be 1.11 weight percent. The additive was believed to be a combination Schiff's base and ester which might be represented by the following formula:



In the above formula x and n have the same significance as in Formula 3, Ar is the naphthalene nucleus and, depending upon the extent to which the naphthalene has been mono- or polyalkylated by the paraffin wax, R is hydrogen or an aliphatic radical derived from paraffin wax.

EXAMPLE 2

To a solution of 36 grams of phthalic anhydride in 400 ml. of orthodichlorobenzene, 37 grams of $AlCl_3$ were added and stirred until a clear yellow solution was formed. Then over a period of one hour, 500 ml. of the wax alkylated naphthalene concentrate of Example 1 were added. Heating was conducted at 150° F. for 6 hours. The product was then freed of aluminum chloride by washing it with acid and water in the same manner as Example 1 and was subsequently heated to 400° F. under reduced pressure (25 inches Hg) to remove orthodichlorobenzene. Then a 188 gram portion of the acid product concentrate thus obtained was mixed with 23 grams of ethylene dinitrilotetraethanol, 200 grams of toluene and 0.1 gram of paratoluene sulfonic acid. The mixture was heated under reflux until no more water appeared in the reflux water trap, indicating the completion of the esterification reaction. Solvent was removed by heating to 210° F. under a reduced pressure of 25 inches of mercury. Analysis of the 50 percent concentrate of additive thus obtained showed a nitrogen content of 0.4 weight percent.

EXAMPLE 3

A wax alkylated phenol is prepared in the following manner: 80 grams of the same chlorinated wax that were employed in Example 1 is mixed with 20.8 grams of phenol and 8 grams of aluminum chloride. The mixture is then heated to about 120° F. for one hour, after which the temperature is raised to 165° F. Then an additional

226.8 grams of the same chlorinated wax are added over a 30-minute period. Following this, the temperature is increased to the range of 285 to 290° F. and held at that point for seven hours. Then the aluminum chloride is removed from the mixture, using hydrochloric acid and water washings in the same manner as described in Example 1. The yield of wax alkylated phenol is about 240 grams.

Then a mixture of 17 grams of aluminum chloride and 200 ml. of normal heptane is prepared and to this is added 12 grams of maleic anhydride at room temperature. After 30 minutes, to this mixture is added 120 grams of wax alkylated phenol prepared as described above. The mixture is heated with stirring for five hours at 150° F. The product is then subjected to washings with hydrochloric acid and water to remove the aluminum chloride in the same manner as described above. Subsequently, the heptane is stripped from the product by heating under vacuum. Then the product is reacted with polyethylene glycol of about 250 molecular weight in approximately equimolar proportions, the esterification reaction being conducted in the presence of about an equal volume of toluene, heating under reflux and collecting the water of esterificaion in a reflux trap in accordance with the usual esterification techniques. The toluene is subsequently removed from the ester product.

EXAMPLE 4

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, the following compositions were prepared:

Composition 1

3.5 weight percent of a commercial detergent inhibitor, 0.9 weight percent of a zinc dialkyldithiophosphate antiwear additive and 95.6 weight percent of the base oil.

Composition 2

3.5 weight percent of the same detergent inhibitor and 0.9 weight percent of the same antiwear additive as in Composition 1, along with 2.0 weight percent of the product of Example 1 and 93.6 weight percent of the base oil.

Composition 3

3.5 weight percent of the same detergent inhibitor and 0.9 weight percent of the same antiwear additive as in Composition 1, along with 2.0 weight percent of the product of Example 2 and 93.6 weight percent of the base oil.

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 is 27 weight percent of phosphosulfurized polyisobutylene, 11.7 weight percent nonyl phenol, 10.6 weight percent barium oxide, 2.5 weight percent carbon dioxide, and 48.2 weight percent of mineral oil.

The zinc dialkyl dithiophosphate antiwear additive was an oil solution consisting of about 25 weight percent of mineral lubricating oil and about 75 weight 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 1500 r.p.m., 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 3½ 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 I. It will be seen from these results that incorporation of the additive products of the present invention greatly increased the ability of the oil composition to disperse sludge.

TABLE I.—SLUDGE MERIT RATINGS—CYCLIC TEMPERATURE TEST

Test Hours	Composition		
	1	2	3
42	8.6		
63	6.9		9.88
84	5.8	10	9.18
105		9.9	8.1
126		9.58	6.2

EXAMPLE 5

Blends were prepared by adding to separate portions of a refined neutral lubricating oil derived from Pennsylvania crude oil sufficient of the concentrate of Example 1 and sufficient of the concentrate of Example 2 to supply 3 weight percent of the additive material in the respective blends. The base oil had a viscosity of 146.7 SUS at 100° F. and of 42.9 SUS at 210° F. A third blend was prepared by adding to another portion of the same base oil sufficient of the wax alkylated naphthalene concentrate of Example 1 to furnish 3 weight percent of wax alkylated naphthalene in the blend.

The pour points of each blend, as well as the pour point of the base oil, were determined. The results are shown in Table II.

TABLE II

	Pour point, ° F.
Base oil	+35
Base oil plus 3% wax alkylated naphthalene [1]	0
Base oil plus 3% Example 1 product [1]	<—35
Base oil plus 3% Example 2 product [1]	<—30

[1] Actual additive basis.

EXAMPLE 6

A lubricant composition suitable for use as a railroad diesel engine lubricant is prepared by blending 2.0 weight percent of the additive concentrate of Example 1 and 0.4 weight percent of phenyl alpha naphthylamine in a base stock consisting of a hydrofined and phenol extracted coastal oil. The blend has a viscosity of 1023 SUS at 100° F.

EXAMPLE 7

To a heating oil comprising a mineral oil distillate having a boiling range of about 350° to 680° F. and derived from mixed cracked and straight run distillates is added 0.02 weight percent of the concentrate product of Example 1.

EXAMPLE 8

A compounded lubricant suitable for use as a crankcase oil is prepared by blending with a light mineral base oil having a sufficient quantity of an added viscosity index improver to place it in the SAE 10W–30 viscosity class, 2.5 weight percent of the concentrate of Example 2, 1.1 weight percent of a high alkalinity barium sulfonate (60 total base number) derived from hydrocarbon sulfonic acids of 440 average molecular weight and 0.65 weight percent of zinc dialkyldithiophosphates derived from mixed C_4, C_5 and C_6 alcohols.

EXAMPLE 9

About 0.007 weight percent of the concentrate of Example 2 is added to a leaded gasoline for the purpose of imparting rust preventive properties and carburetor detergency action thereto.

The additives of this invention may be employed in concentrations ranging from about 0.002 to about 10 weight percent in oleaginous 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 weight percent and will ordinarily be used in concentrations of from about 0.1 to about 5 weight 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 type, 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 weight percent or more, generally from about 0.005 to about 0.2 weight percent, are employed. Petroleum distillate fuels boiling in the range of from about 300° 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. 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 weight percent as detergents and/or rust preventive additives.

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 3 to 8 carbon atoms, antioxidants such as phenyl-alpha-naphthylamine, tertiary octylphenol sulfide, bis-phenols such as 4,4'-methylene bis (2,6-di tertiary butylphenol), viscosity index improvers such as polymethacrylates, polyisobutylene, alkyl fumarate-vinyl acetate copolymers, and the like, as well as other dispersants.

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 weight 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 earth metal sulfonates, and dispersions of barium carbonate or calcium carbonate in mineral oils containing various surfactants such as phosphosulfurized polyolefins, for example.

The sulfonates are well known in the art and are the oil-soluble alkaline earth metal salts of high molecular weight sufonic acids obtained by sulfonating either natural or synthetic hydrocarbons. Specific examples of suitable sulfonates include calcium petroleum sulfonate, barium petroleum sulfonate, calcium di-C_9 alkyl benzene sulfonate (C_9 group from tripropylene), and barium C_{16} alkyl benzene sulfonate (C_{16} group from tetraisobutylene). The sulfonates may be of either the neutral type or of the "over-based" or "high alkalinity" type, containing metal base in excess of that required for simple neutralization, wherein the excess metal base has been neutralized with carbon dioxide.

Metal salts of alkyl phenols and of the alkyl phenol sulfides are also well known in the art. Metal salts of alkyl phenols having alkyl groups of from 5 to 20 carbon atoms are usually preferred, and the metal used to form the phenate is preferably an alkaline earth metal, e.g. calcium or barium, although the salts such as those of aluminum, cobalt, lead or tin are sometimes used. A specific example is the barium salt of the alkylation product of phenol with tripropylene. Metal salts of the corresponding alkyl phenol sulfides may also be used, e.g. barium tertiary octyl phenol sulfide.

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 weight percent of mixed C_9 to C_{12} fumarates, 10 to 20 weight percent of vinyl acetate, and 5 to 15 weight percent of N-vinyl pyrrolidone. Another example is the copolymer derived by reaction of mixed tallow alcohol fumarates and C_8 oxo alcohol fumarates, averaging about 420 molecular weight, with vinyl acetate in a 3 to 1 acetate-fumarate ratio, and 3 weight percent of maleic anhydride, followed by subsequent removal of excess vinyl acetate. By tallow alcohol fumarates is meant the esters of fumaric acid and the alcohols derived by hydrogenation of tallow. The latter are principally C_{16} and C_{18} aliphatic alcohols with minor amounts of C_{12}, C_{14} and C_{20} alcohols. C_8 oxo alcohols are prepared by reaction of carbon monoxide and hydrogen on mixed C_3 to C_4 olefins followed by hydrogenation of the resulting aldehydes.

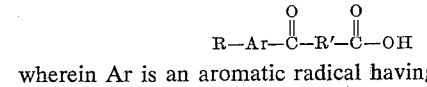
It is within the contemplation of this invention to prepare additive concentrates in which the concentration of additive is greater than would normally be employed in a finished lubricant. These concentrates may contain in the range of from 10 to 80% of additive on an active ingredient basis, the balance being 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. Thus, if the additives are to be used in conjunction with conventional detergents, an additive concentrate can be prepared containing say 30 to 60 weight percent of an additive of the invention and 5 to 20 weight percent of a metal sulfonate, e.g. calcium petroleum sulfonate from sulfonic acids of about 450 molecular weight, or a metal alkylphenol sulfide, e.g. calcium nonylphenol sulfide, with the balance being a mineral lubricating oil. Additionally, 5 to 15 weight percent of an antiwear agent such as a zinc dialkyldithiophosphate, e.g. mixed zinc butyl and amyl dithiophosphates may also be present in the additive concentrate package.

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 understood that the examples presented herein are intended to be merely illustrative of the invention and not as limiting it in any manner; nor is the invention to be limited by any theory regarding its operability. The scope of the invention is to be determined by the appended claims.

What is claimed is:

1. A method for preparing an oil-soluble additive for an oleaginous composition which comprises reacting from 1 to 2 moles of an alkaryl keto acid with 1 mole of a polyhydroxy compound under conditions forming an ester of said acid, said polyhydroxy compound being selected from the group consisting of: polyhydric alcohols having from 2 to 10 carbon atoms and from 2 to 6 hydroxy groups; polyalkylene glycols of from 100 to 600 molecular weight; and polyhydroxy alkyl amines having from 5 to about 30 carbon atoms, from 2 to 6 hydroxy groups and from 1 to 4 tertiary amino groups, said aryl keto acid having the general formula:



wherein Ar is an aromatic radical having in the range of 6 to 16 carbon atoms, R is at least 1 aliphatic hydrocarbon radical having in the range of from 12 to 30 carbon atoms, and R′ is a hydrocarbon linkage having in the range of from about 2 to 18 carbon atoms.

2. A method as defined by claim **1** wherein said keto acid has been obtained by alkylating an aryl compound from the class consisting of cyclic hydrocarbons and hydroxy derivatives thereof with an aliphatic hydrocarbon of from 12 to 30 carbon atoms and condensing the alkylated aryl compound with a dibasic acid compound having in the range of from 4 to 20 carbon atoms and selected from the group consisting of dibasic acids, dibasic acid anhydrides, dibasic acid monohalides and dibasic acid dihalides.

3. A method as defined by claim **2** wherein said keto acid has been obtained from a paraffin-wax-alkylated naphthalene.

4. A method as defined by claim **1** wherein said keto acid has been obtained by condensation of a paraffin-wax-alkylated naphthalene with maleic anhydride.

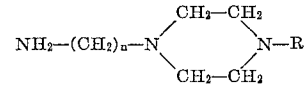
5. A method as defined by claim **1** wherein said keto acid has been obtained by condensation of a wax-alkylated phenol with maleic anhydride.

6. A method as defined by claim **1** wherein said keto acid has been obtained by condensation of a wax-alkylated naphthalene with phthalic anhydride.

7. A method as defined by claim **1** including the additional step of reacting the said ester with an aliphatic polyamine selected from the class consisting of N,N-di(2-aminoethyl) ethylene diamine, alkylene polyamines having the formula:

$$NH_2(CH_2)-[NH(CH_2)_n]-NH_2$$

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



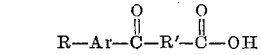
wherein n is a number 1 to 3, and R is selected from the group consisting of hydrogen and aminoalkyl radicals containing 1 to 3 carbon atoms, said additional step being conducted under conditions forming a Schiff's base derivative with said polyamine.

8. A method as defined by claim **7** wherein said aliphatic polyamine is tetraethylene pentamine.

9. The product obtained by the method of claim **1**.

10. The product obtained by the method of claim **7**.

11. An oil-soluble dispersant additive for oleaginous compositions which comprises the product obtained by reacting a polyhydroxy compound with an alkaryl keto acid, under ester forming conditions, using a molar proportion of acid to polyhydroxy compound in the range of about 1 to 1 to about 2 to 1, said aralkyl keto acid having the general formula



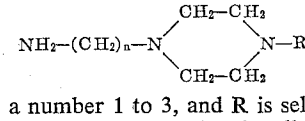
wherein R is at least 1 aliphatic hydrocarbon radical having in the range of 12 to 30 carbon atoms, R′ is a hydrocarbon linkage having in the range of about 2 to 18 carbon atoms, and Ar is an aromatic radical selected from the group consisting of cyclic hydrocarbons, short-chain-alkylated cyclic hydrocarbons, and hydroxy derivatives of said cyclic hydrocarbons, said aromatic radical having in the range of 6 to 16 carbon atoms, said polyhydroxy compound being selected from the group consisting of: polyhydric alcohols having from 2 to 10 carbon atoms and from 2 to 6 hydroxy groups; polyalkylene glycols of from 100 to 600 molecular weight; and polyhydroxy alkyl amines having from 5 to about 30 carbon atoms, from 2 to 6 hydroxy groups and from 1 to 4 tertiary amino groups.

12. Additive as defined by claim **11** wherein R represents an alkyl radical derived from halogenated paraffin wax.

13. An oil-soluble dispersant additive for oleaginous compositions which comprises the product obtained by further reacting the product defined by claim **11** with an aliphatic polyamine, under conditions forming a Schiff's base derivative, said aliphatic polyamine being selected from the class consisting of N-N-di(2-aminoethyl) ethylene diamine, alkylene polyamines having the formula:

$$NH_2(CH_2)_n-[NH(CH_2)_n]_m-NH_2$$

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 containing 1 to 3 carbon atoms.

14. An oil-soluble dispersant additive for oleaginous compositions which comprises the ester reaction product of ethylene dinitrilotetraethanol and an alkaryl keto acid obtained by condensation of wax-alkylated naphthalene with phthalic anhydride.

15. An oil-soluble dispersant additive for oleaginous compositions which comprises the product obtained by reacting, under ester-forming conditions, ethylene dinitrilotetraethanol with an alkaryl keto acid obtained from paraffin-wax-alkylated naphthalene and maleic anhydride, and further reacting the ester obtained thereby, with tetraethylene pentamine under conditions forming a Schiff's base derivative.

16. An oleaginous composition comprising a major proportion of an oil selected from the class consisting of gasoline, middle distillate fuels, mineral lubricating oils and synthetic lubricating oils to which has been added from about 0.002 to about 10 weight percent of the product of claim 1.

17. An additive concentrate comprising a mineral oil containing from 10 to 80 weight percent of the product of claim 1.

18. A lubricating oil composition comprising a major proportion of a lubricating oil to which has been added from about 0.1 to about 10 weight percent of the product of claim 1.

References Cited by the Examiner

UNITED STATES PATENTS

2,094,453	9/1937	Jaeger	260—469
2,589,224	3/1952	Burtner	260—472
2,642,455	6/1953	Bruins et al.	260—469
2,897,230	7/1959	Dazzi.	
3,142,692	7/1964	Maggiulli et al.	260—469 X
3,181,938	5/1965	Eckert et al.	44—70 X

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