Protection against corrosion and deposition of sludge and varnish is provided by lubricating oils containing a minor amount of the ashless type addition agents which are prepared by reacting under conditions of the Mannich Reaction (1) a high molecular weight alkyl-substituted hydroxy aromatic compound, in which the alkyl-substituent has an average molecular weight of from about 600 to about 100,000, (2) an amine compound containing at least one \( \text{HN} \) group, (3) an aliphatic aldehyde, and (4) an aliphatic acid containing at least six carbon atoms, in the respective reactant molar ratio of 1:0.1-10:1-10:0.014-1.0 and further reacting such modified condensation product with from about 2 to about 6 moles of an aliphatic aldehyde per mole of the alkyl-substituted hydroxy aromatic compound.

10 Claims, No Drawings
OIL SOLUTION OF ALIPHATIC ACID AND ALIPHATIC ALDEHYDE MODIFIED HIGH MOLECULAR WEIGHT MANNICH REACTION PRODUCTS

RELATED APPLICATIONS

This application is a division of copending application Ser. No. 68,469, filed Aug. 31, 1970, which is a continuation-in-part of copending application Ser. No. 54,558, filed July 13, 1970.

BACKGROUND OF THE INVENTION

This invention relates to improved lubricating oils and particularly concerns automobile and Diesel crankcase lubricating oil formulations containing a minor amount of a low class of oil-soluble addition agents which improve the performance of the oil, particularly its dispersant-detergent function thus enabling lubricating oils to provide a high degree of protection of the lubricated parts of internal combustion engines.

Present-day automobile and Diesel engines have been designed for higher power output, lower combustion products emission and longer in-service periods of use of crankcase lubricating oils. These design changes have resulted in such severe operating conditions as to necessitate devising higher efficiency lubricating oils that will, under the increased severity of in-service use, afford proper protection against corrosion and the accumulation or deposition of sludge, varnish and resinous materials on the surface of engine parts which rapidly accelerate decrease in both operating efficiency and life of the engine. The principal ingredient of crankcase lubricants is a base lubricating oil, a mixture of hydrocarbons derived from petroleum. Even when highly refined by removal of deleterious components, such as polymerizable components, acid formers, waxes, etc., a lubricant base oil still requires the addition of a number of oil soluble chemical additives to enable the oil to resist oxidation, deposition of sludge and varnish on, and corrosion of, the lubricated metal parts, and to provide added lubricity and regulated viscosity change from low to high temperature. These ingredients are commonly known as anti-oxidants, dispersant-detergents, pour point dispersants, etc.

Combustion products from the burning of fuel and thermal degradation of lubricating oils and addition agents tend to concentrate in the crankcase oil with the attendant formation of oil-insoluble deposit-forming products, that either surface coat the engine parts (varnish or lacquer-like films) or settle out on the engine parts as viscous (sludge) deposits or form solid ash-like or carbonaceous deposits. Any of such deposits can restrict, and even plug, grooves, channels and holes provided for lubricant flow to the moving surfaces of the engine requiring lubrication thus accelerating the wear and thus reducing the efficiency of the engine. In addition, acidic combustion products corrode the lubricated metal surfaces. Chemical additives are blended in crankcase oil formulations not only to reduce thermal decomposition of the oil and addition agents (anti-oxidants) but also to keep in suspension (as a dispersant) and to suspend (as a detergent) insoluble combustion and degradation products as well as to neutralize acidic products (anti-corrosion agents). A separate additive is usually added for each improvement to be effected.

As performance levels increased and recommended periods between oil drains lengthened for both automobile and railway Diesel engines, more efficient dispersancy and detergency performance, as well as better acid neutralization and lower ash-forming properties were demanded for lubricating oil formulations. Among additives suggested by the prior art are amine salts, amides, imides, and amidines of polybutenyl-substituted polycarboxylic acids and polymeric compounds having pendant or grafted-on polar groups. Other suggested prior additives are combinations of alkali earth metal sulfonates and Mannich condensation products of low molecular weight alkyl (C₇-C₂₀) substituted hydroxyaromatic compounds, amine having at least one replaceable hydrogen on a nitrogen and aldehydes; and, alkali earth metal salts of such Mannich condensation products. These prior art products did not provide the desired dispersancy-detergency properties and possessed the objectionable property of forming harmful metal-ash deposits.

Mannich condensation products derived from alkyl-substituted hydroxyaromatic compounds having a relatively low molecular weight alkyl substituent, i.e., two to 20 carbon atoms in the alkyl substituent and chlorinated wax (straight chain) type alkyl-substituents are described in U.S. Pat. Nos. 2,403,453; 2,353,491; 2,563,134; 2,459,112; 2,984,550 and 3,036,003. However, none of such prior Mannich condensation products are suitable for use as dispersant-detergent additives agents for present-day long drain oil interval in-service use.

One known type (U.S. Pat. No. 2,363,134) has been prepared by reacting, under Mannich reaction conditions, equimolar quantities of a C₆-C₉ alkyl-substituted phenol and other hydroxy aromatic compounds, and N,N-di-substituted amine and formaldehyde.

The prior C₇-C₂₀ alkyl-substituted Mannich condensation products commonly are prepared by the conventional technique of adding the aliphatic aldehyde to a heated mixture of the alkylhydroxyaromatic and amine reagents, in the presence or absence of a solvent, and then heating the resultant mixture to a temperature between 100°-350°F. until dehydration is complete. A solvent such as benzene, toluene, xylene, methanol and others easily separated from the reaction mixture and light mineral oils, such as those used in blending stocks to prepare lubricating oil formulations in which the product is formed as a mineral oil concentrate are usually used. The water by-product is removed by heating the reaction mixture to a temperature sufficiently high, at least during the last part of the process, to drive off the water alone, or as an azeotropic mixture with the aromatic solvent, usually by the aid of an inert stripping gas, such as nitrogen, carbon dioxide, etc.

The neutralized or overbased alkali earth metal salts (alkaline earth metal phenates) of those prior low molecular weight Mannich condensation products have been suggested for use in providing lubricating oils with a combination of detergent-inhibitor properties in one addition agent. The neutralized alkaline earth metal salts have one equivalent of alkaline earth metal for each hydroxy group present. The overbased salts have, for each hydroxy group present, more than one equivalent of alkaline earth metal in the form of a hydroxy metaloxy, alkoxy metaloxy and even alkaline earth
metal carbonate complex with hydroxy metaloxy on each benzene group as a replacement for the phenol hydroxy group. As noted, above, said addition agents form objectionable metal ash deposits and have other performance deficiencies.

U.S. Pat. No. 3,368,972 issued Feb. 13, 1968 describes as dispersant-detergent addition agents for lubricating oils high molecular weight Mannich condensation products from (1) high molecular weight alkyl-substituted hydroxysteromatic compounds whose alkyl-substituent has a molecular weight in the range of 600-3000, (2) a compound containing at least

\[
\text{one } \text{HN group}
\]

and (3) an aldehyde in the respective molar ratio of 1.0:0.1-10:1.0-10.

The high molecular weight Mannich condensation products of U.S. Pat. No. 3,368,972 have a drawback in their large-scale preparation and in their extended service use as lubricant addition agents used under high temperature conditions such as encountered in diesel engines. In the large-scale or plant preparation of such high molecular weight condensation products, especially in light mineral oil solvents, the resulting oil concentrate solution of the condensation product either has or develops during storage a haze which is believed to be caused by undissolved or border line soluble byproducts which not only are substantially incapable of removal by filtration but also severely restrict product filtration rate. When used in diesel engine crankcase lubricant oils and subject to high temperature in service use, piston ring groove carbonaceous deposits and skirt varnish tend to build up sufficiently rapidly and prevent desirable long in service use of such lubricant oils.

As taught and claimed in our aforesaid co-pending application, both of these drawbacks are overcome by modifying the high molecular weight Mannich condensation products with an aliphatic acid having at least six carbon atoms. While such modification of such Mannich condensation products overcomes the aforementioned drawbacks, such modified Mannich products do not possess the desired thermal oxidation stability. We have now discovered that the storage and thermal stability of such aliphatic acid-modified high molecular weight Mannich condensation products are improved by treating such condensation products with an additional amount of an aliphatic aldehyde.

**BRIEF SUMMARY OF THE INVENTION**

This invention pertains to lubricant oil compositions comprising a major amount of lubricating oil and a minor amount, 0.01 to 10 weight percent, of a new class of compounds useful as multifunctional addition agents for lubricating oils, particularly such oils used in internal combustion engines in which they function as highly efficient dispersant-detergent and oxidation inhibitor agents.

The new class of compounds which comprise the addition agent component of this invention are oil-soluble high molecular aliphatic acid modified high molecular weight products of the Mannich Reaction which are further treated with an aliphatic aldehyde. They can be made by condensing in the usual manner under conditions of the Mannich Reaction.

1. an alkyl-substituted hydroxysteromatic compound, in which the alkyl-substituent has an average molecular weight of about 600-100,000, preferably a polyalkylphenol whose polyalkyl substituent is derived from 1-

mono-olefin polymers having an average molecular weight of about 850-2500;

2. an amine containing at least

\[
\text{one } \text{NH group}
\]

preferably an alkylene polymine of the formula

\[
\text{NH}_{x} \left( \text{A-N} \right)_{1-x} \text{H}
\]

wherein A is a divalent alkylene radical having two to six carbon atoms, and x is an integer from 1 to 10;

3. an aliphatic aldehyde, preferably formaldehyde or paraformaldehyde; followed by reaction with;

4. an high molecular weight aliphatic acid before or after filtration; or they can be prepared by using all four reactants at one time under the general conditions of the Mannich Reaction.

The above resultant modified products of the Mannich Reaction are then treated with (5) an aliphatic aldehyde in an amount of from about 2 to about 6 moles of the aldehyde per mole of the alkyl-substituted hydroxy compound used in the preparation of said modified Mannich Reaction product.

The foregoing high molecular weight products of this invention are preferably prepared according to the conventional methods employed for the preparation of Mannich condensation products, using the first four above mentioned reactants in the respective molar ratios of about 1.0:0.1-10:1.0-10:0.014-1.0. Suitable condensation procedure involves adding at a temperature of from room temperature to about 200°F the aldehyde reagent (3) to a mixture of reagents (1), (2), and (4), above, or such reagents in an easily removed organic solvent, such as benzene, xylene, or toluene, or in a solvent refined mineral oil; completing the reaction at 300°F.; then slowly adding the additional aldehyde, reactant (5) at 180°-300°F. The reaction mass is then heated at an elevated temperature of about 275°-375°F. preferably with blowing with an inert stripping gas, such as nitrogen, carbon dioxide, etc. until dehydration is complete.

The preferred additives, according to this invention, are high molecular weight bis-Mannich condensation products formed by reacting (1) a 850-2,500 molecular weight polybutylyphenol; (2) an ethylene polyamine; (3) formaldehyde; and (4) an aliphatic acid in the respective molar ratio of 1.0:0.7-1.0:1.5-2.1:0.014-0.62, and treating the resultant modified Mannich condensation product with 2-4 moles of paraformaldehyde per mole of the polybutylyphenol. The preferred aliphatic acid reactant is an acid having 10-20 carbon atoms per carboxylic acid group.

To those skilled in the art, it will be recognized that, in general, the condensation reaction under the Mannich Reaction conditions, as in other chemical reactions, does not go to theoretical completion, and some portion of the reactants remain unreacted or only partially reacted as co-products. Accordingly, the products of this invention cannot be properly or accurately characterized with preciseness by chemical structural formula, but must be characterized as reaction products produced by the method of preparation.

The high molecular weight products of this invention are effective additives for lubricating oil lubricants, imparting thereto dispersant-detergent properties and high temperature oxidation stability, at relatively low
concentrations, e.g., 0.05 to about 10 percent in formulated crankcase lubricating oil compositions. Higher concentrations, e.g., 10 to about 70 percent, are useful concentrates for the preparation of such lubricating oil compositions.

For a more complete understanding of the Mannich Reaction reference is made to Organic Reactions, Vol. 1, pages 303-341 (1942) publication of John Wiley and Sons, Inc.

EMBODIMENT OF THE INVENTION

Representative lubricating oils for the lubricant oil compositions of this invention include the normally liquid oleaginous lubricants which are hydrocarbon fractions derived from petroleum and synthetic ester or alkylene oxide type lubricants having the viscosity within the range represented by SAE 5 to SAE 50 weight mineral oils. Such lubricating oils can be single oils within said viscosity range or mixtures of such oils as well as mixtures of such mineral oils with a synthetic type lubricant. For use in automobile and diesel engines it is preferred that the lubricant oil compositions contain a major amount of said mineral oil derived from petroleum and said mineral oil can be a petroleum fraction or the hydrogenated derivative thereof. There can also be present and preferably is present when more than one viscosity lubricant comprises the lubricant oil major portion, a viscosity index (VI) improver such as the rather viscous, oil polybutene VI improver and/or the polycarbonate type VI improver.

Representative high molecular weight aliphatic acid modified Mannich condensation products contemplated by this invention can be prepared from the following representative reactants of the classes before defined.

1. High Molecular Weight Alkyl-Substituted Hydroxyaromatics

Representative of these high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylene, polybutylenephenol and other polyalkylphenols. These polyalkylphenols may be obtained by the alkylation, in the presence of an alkylating catalyst, such as BF₃, of phenol with high molecular weight polypropylene, polybutylene and other polyalkylene compounds to give alkyl substituents on the benzene ring of phenol having an average 600-100,000 Mn. Their preparation using a BF₃ phenol catalyst is described and claimed in our copending application Ser. No. 484,758, filed Sept. 2, 1965.

The 600 Mn and higher Mn alkyl-substituents on the hydroxyaromatic compounds may be derived from high molecular weight polypropylenes, polybutenes and other polymers of mono-olefins, principally 1-mono-olefins. Also useful are copolymers of mono-olefins with monomers copolymerizable therewith wherein the copolymer molecule contains at least 90 percent, by weight, of mono-olefin units. Specific examples are copolymers of butenes (butene-1, butene-2 and isobutylene) with monomers copolymerizable therewith wherein the copolymer molecule contains at least 90 percent, by weight, of propylene and butene units, respectively. Said monomers copolymerizable with propylene or said butenes include monomers containing a small proportion of unreactive polar groups such as chloro, bromo, keto, ether, aldehyde, which do appreciably lower the oil-solubility of the polymer. The copolymers polymerized with propylene or said butenes may be aliphatic and can also contain non-aliphatic groups, e.g., styrene, methylstyrene, p-dimethylstyrene, divinyl benzene and the like. From the foregoing limitations placed on the monomer copolymerized with propylene or said butenes, it is abundantly clear that said polymers and copolymers of propylene and said butenes are substantially aliphatic hydrocarbon polymers. Thus the resulting alkylated phenols contain substantially alkyl hydrocarbon substituents having Mn upward from 600.

In addition to these high molecular weight hydroxyaromatic compounds others which may be used include those which have been used to prepare prior low molecular weight Mannich condensation products, e.g., high molecular weight alkyl-substituted derivatives of resorcinol, hydroquinone, cresol, catechol, xylenol, hydroxy diphenyl, benzylphenol, phenethylphenol, naphthol, tollynaphtol, among others. Preferred for the preparation of the aforementioned preferred bis Mannich condensation products are the polychlorophenyl reagents, e.g., polychloropropyl and polybutylphenol whose alkyl group has an average number molecular weight of 600-3,000, the most preferred being polybutylphenol whose alkyl group has an average number molecular weight of 850-2500.

(2) HN- Group Containing Reactants

Representative of this class of reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one HN-group are suitable for use in the preparation of Mannich condensation products are well known and include the mono- and di-amino alkanes and their substituted analogs, e.g., ethylamine and diethanol amine; aromatic diamines, e.g., phenylene diamine, dianime naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrroli dine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs. Suitable alkylene polyamine reactants include ethylene diamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylene hexamine, hexaethylene hepta-amine, heptaethylene octamine, octaethylene nonamine, nonaethylene decamine and decaethylene undecamine and mixture of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula H₂N-(A-NH)₄H, mentioned before A is divalent ethylene and x is 1 to 10 of the following formula. Corresponding propylene polyamines such as propylene diamine and di-, tri-, tetra-, penta-, propylene tri-, tetra-, penta- and hexaamines are also suitable reactants. The alkylene polyanines are usually obtained by the reaction of ammonia and dihala alkanes, such as dichloro alkanes. Thus the alkylene polyamines obtained from the reaction of 2 to 11 moles of ammonia with 1 to 10 moles of dichloro alkanes having two to six carbon atoms and the chlorines on different carbons are suitable alkylene polyamine reactants.

ALDEHYDE REACTANTS

Representative of this aldehyde class of reactants for use in the preparation of the high molecular products of this invention include the aliphatic aldehydes such as
formaldehyde (also as paraformaldehyde and formalin), acetaldehyde and aldo (b-hydroxybutyraldehyde). We prefer to use formaldehyde, para-formaldehyde or a formaldehyde yielding reactant.

**ALIPHATIC ACID REACTANTS**

The aliphatic acid reactant of this invention has a carbon atom content of a total (including the carbon of the carboxylic acid group) of from about six to about 30 and consists of the aliphatic (saturated) and alkenoic (mono-unsaturated) acids. The upper limit of the carbon content is restricted only by the largest carbon atom content of such acids available or capable of feasible preparation. Such aliphatic acids can be natural and synthetic mono-, di- and tri-carboxylic acids. Suitable natural aliphatic acids are the natural fatty acids obtainable by known hydrolysis (acid and alkaline) of vegetable and animal oils and fats and wax esters. Of those natural acids for the purposes of this invention the preferred acids have from 10 to about 20 total carbon atoms per carboxylic acid group. Suitable synthetic acids can be derived from oxidation of the alcohol moiety of the wax ester where such alcohol moiety has at least six carbon atoms; from the polymerization of unsaturated natural acids having two or three carbon to carbon double bonds (dimer and trimer acids) and the hydrogenation of residual carbon to carbon double bonds in such polymer acids. For example the polymer acids obtained from oleic acid, acric acid, linoleic acid and linolenic acid and other unsaturatated acids; and from oxidation or other reactions of polypropenes and polybutenes (e.g. polisobutenes) which introduce one or more carboxylic acid group on the polymer chain.

It might be expected that the high molecular weight Mannich product modified by an unsaturated aliphatic carboxylic acid such as oleic acid or its C16 unsaturated homolog would have less oxidation stability than for example such Mannich products modified by a saturated aliphatic acid such as stearic acid. But this, somewhat unexpectedly, is not the case. For example in a standard oxidation stability test (Union Pacific Oxidation Test) there are tested oil formulations containing equivalent amounts of high molecular weight Mannich Product (a polybutyl-1, hydroxybenzyl-substituted tetraethylene pentamine having a number average molecular weight of 3,600) and the same Mannich Product modified with 0.125 mole (0.8 weight percent) of each of oleic acid, isostearic acid, a mixture of C18 and C19 monounsaturated alkenoic acids and a mixture of C16 and C18 saturated alkenoic acids. The pentane insolubles content of these tests, indicative of oxidation stability, is measured and is as follows:

<table>
<thead>
<tr>
<th>Additive</th>
<th>Acid Modifier</th>
<th>Pentane Insolubles - Gms.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mannich Product</td>
<td>none</td>
<td>1.5</td>
</tr>
<tr>
<td>Ditto</td>
<td>oleic acid</td>
<td>2.5</td>
</tr>
<tr>
<td>Ditto</td>
<td>isostearic acid</td>
<td>3.0</td>
</tr>
<tr>
<td>Ditto</td>
<td>C16+C18 mixtures of monounsaturated acids</td>
<td>3.0</td>
</tr>
<tr>
<td>Ditto</td>
<td>C16+C18 mixture of saturated acids</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Suitable alkenoic acids having six or more total carbon atoms are those obtainable from the glycerides: vegetable oils and animal fats and the wax esters by the known hydrolysis or saponification-acidification or acid treatment processing of said oil and fat glycerides and the wax esters, i.e., natural waxes, the oxidation of the mono-alcohol obtainable from the simple ester of the wax esters and known acid synthesis. Such suitable alkenoic acids, i.e., having R groups of six to 30 carbon atoms, include caproic acid, caprylic acid, capric acid, heptadecyl acid, lauric acid, tridecyl acid, myristic acid, pentadecyl acid, palmitic acid, margaric acid, stearic acid, nonadecyl acid, arachidic acid, medullic acid, behenic acid, lignoceric acid, pentacosioic acid, cerotic acid, heptacosioic acid, monocosioic acid, montanic acid, and melissic acid. Many of said alkenoic acids are obtained first in mixtures of two, three or more alkenoic acids of different carbon contents from said glycerides and wax esters; said mixtures can be used in this invention in place of a single alkenoic acid reactant. When said mixtures of alkenoic acids also contain unsaturated acids it is preferred that such mixture of acids be reduced to a product which is substantially free of unsaturation.

Suitable alkenoic acids having a total of at least six carbon atoms include those from hexenoic, heptenoic, octenoic, etc. acids up to oleic (C18) and erucic (C22) acids. Also suitable are the dimer acid of linoleic and its saturated dimer analog; dimer and trimer acids of linolenic acid and the saturated dimer and trimer analogs. Other polymeric acids, e.g. co-dimers of oleic and linoleic or linolenic acids and the saturated analogs of those dimer acids are also suitable.

The foregoing, while not an exhaustive listing of all suitable aliphatic acid reactants of the class before defined, will provide adequate guidance for the chemist skilled in this art and also bring to mind other suitable aliphatic acids within the scope before defined. The following examples are illustrative of preferred embodiments of the present invention:

**EXAMPLE I**

2085 grams (0.61 mole) of a 1,600 average molecular weight polyaryl-substituted phenol (47 percent polybutylphenol, 53 percent polybutene and diluent oil), 765 grams of a solvent-extracted 5W mineral oil, 109 grams (0.56 mole) tetraethylene pentamine, and 109 grams (0.38 mole) of a modified saturated C16-C18 fatty acid, identified as "Emery 896 Fatty Acid" by Emery Industries Inc., were admixed and heated to 150°F. 84 cc. (1.12 moles) of formalin were then rapidly added to the mixture. Thereafter, there were slowly added 168 cc. (2.24 moles) of formalin over a 1.5 hour period, during which time the reaction temperature was allowed to rise to 200-220°F. Upon completion of the formaldehyde addition, the reaction mixture was heated to a temperature of 300°-320°F. and held at such temperature for 3 hours while blowing with nitrogen at a rate of 2 cubic feet per hour (CFH). At the end of three hours the reaction mass was filtered. The recovered filtrate was clear, had a nitrogen content of 1.30 percent, and a SSU viscosity at 210°F. of 954.
EXAMPLE II
Part A. 2370 grams (0.73 mole) of a 1,526 average molecular weight polybutyl-substituted phenol (49.4 percent polybutylphenol, 50.6 percent polybutene and oil), 300 grams of a solvent-extracted 5W mineral oil, 128 grams (0.454 mole) oleic acid, and 127 grams (0.672 mole) tetraethylene pentamine were admixed at 150°F., and 100 ccs. (1.344 mole) formaldehyde added. The temperature was increased to 300°-320°F., while blowing with nitrogen at 2 CFH, and maintained at such temperature for 2 hours. 489 grams of a solvent-extracted 5W mineral oil were added to the reaction product.

Part B. To 3200 grams of an oleic acid-modified Mannich condensation product prepared as in Part A, above, were added at 300°F. 90 grams (2.8 moles) paraformaldehyde, and 140 grams of a solvent-extracted 5W mineral oil, and the mixture maintained at 300°-320°F. for 3 hours while blowing with nitrogen at the rate of 2 CFH. The reaction product was then filtered.

Three other batches were prepared as the above, and the four batches combined. The composite product was crystal clear and had a SSU viscosity at 210°F. of 1,028.

The thermal oxidation stability of the aldehyde treated acid-modified high molecular weight Mannich condensation product is demonstrated by the so-called "Hot Tube Test." This test measures the oxidation and thermal stability of dispersant additives for lubricating oils, particularly automotive crankcase lubricants. In making this test the subject dispersant is incorporated in a typical crankcase lubricating oil composition formulation, and the composition subjected to the following test: The oil composition being tested is passed, at the rate of 0.1 cc. per minute downward through a 20 inch, 8 mm. vertical glass tube 6 inches of which are surrounded by a furnace and heated at 495°F. for 100 minutes, while air at the rate of 20 ccs. per minute is passed downwardly through the tube. At the end of the 100 minute test period the tube is cooled and rinsed with hexane, and the appearance of the tube evaluated as to varnish area and intensity. A perfect tube is rated "10A," where the numerical value refers to the varnish in the heated portion of the tube, and the letter rating refers to the varnish formed in the cool zone of the tube below the furnace. The lower the numerical rating and the higher the letter rating, the poorer is the oxidation and thermal stability of the dispersant.

The data in Table I, below, were obtained by subjecting the following lubricating oil formulations to the above "Hot Tube Test":

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hot Tube Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7.8D</td>
</tr>
<tr>
<td>B</td>
<td>8.2C</td>
</tr>
<tr>
<td>C</td>
<td>8.0B</td>
</tr>
</tbody>
</table>

The letter rating "B" in the above test indicates that the aldehyde treated acid-modified Mannich condensation product (Sample C), exhibits better thermal oxidation stability than the acid-modified Mannich product, (Sample B), which had a letter rating of "C."

As noted hereinbefore, the product of the present invention are useful additive agents for lubricating oils. Such oils can be any normally liquid oleaginous lubricants, such as hydrocarbon oils, both natural, i.e., petroleum oils, and synthetic lubricating oils, for example, those obtained by the polymerization of olefins, as well as synthetic lubricating oils of the alkylene oxide type, and the polyalcoholic acid ester type, such as the oil-soluble esters of adipic acid, sebacic acid, azelaic acid, etc.

Lubricating oil compositions containing the aldehyde treated acid-modified Mannich condensation products of the present invention, may also contain other additives such as, for example, VI improvers, rust inhibitors, oiliness agents, pour point depressors, etc.

Percentages given herein and in the appended claims are weight percentages unless otherwise stated.

Although the present invention has been described with reference to specific preferred embodiments thereof, the invention is not to be limited thereto, but includes within its scope such modifications and variations as come within the scope and spirit of the appended claims.

What is claimed is:

1. A lubricant oil composition comprising a major amount of normally liquid oleaginous lubricant and a minor detergent-dispersant amount of an oil-soluble aliphatic acid and aliphatic aldehyde modified high molecular weight product of the Mannich Reaction conducted first at a temperature within the range of 150° to 325°F. with the reactants:
   a. a high molecular weight alkyl-substituted hydroxy- aromatic compound wherein the alkyl substituent has an average molecular weight of from about 600 to about 100,000;
   b. an amine containing at least one HN group;
   c. an aliphatic aldehyde; and
3,793,202

d. saturated or unsaturated aliphatic acid containing from six to 30 carbon atoms or polymers of such unsaturated acid in the respective reactant molar ratio of 1.0: 0.1–10:1.0–10: 0.14–1.0, then with slow addition to the resultant first product of e. additional aliphatic aldehyde in the molar ratio of from about 2 to about 6 moles of the additional aldehyde per mole of said reactant (a), increasing the temperature of the resultant reaction mass to within the range of 275°F. to 375°F., and stripping with inert gas to dehydrate the resultant product.

2. The lubricant oil composition of claim 1 wherein said minor detergent-dispersant amount is within the range of 0.05 to 10 weight percent.

3. The lubricant oil composition of claim 2, wherein the high molecular weight alkyl-substituted hydroxyaromatic compound is a polyalkyl-substituted phenol, wherein the polyalkyl-substituent has a molecular weight of from about 600 to about 3,000.

4. The lubricant oil composition of claim 2, wherein the amine is selected from the group consisting of polyalkylamines and polyalkenepolyamines.

5. The lubricant oil composition of claim 4, wherein the polyalkenepolyamine is tetraethylene pentamine.

6. The lubricant oil composition of claim 2, wherein the aliphatic aldehyde (c) is formaldehyde, and the additional aldehyde (e) is paraformaldehyde.

7. The lubricant oil composition of claim 2, wherein the aliphatic acid is oleic acid.

8. The lubricant oil composition of claim 2 wherein the first reactants are:
a. polybutyl-substituted phenol wherein the polybutyl-substituent has an average molecular weight of from about 600 to about 3,000;
b. ethylene polyamine;
c. formaldehyde; and
d. oleic acid used in the respective reactant molar ratio of 1:0.7–1.0:1.5–2.1:0.014–1.0 and
e. the additional aliphatic aldehyde is paraformaldehyde.

9. The lubricant oil composition of claim 8, wherein the (a) polybutyl has the polybutyl substituent of average molecular weight of about 1,500, (b) ethylene polyamine is tetraethylene pentamine, (c) formaldehyde is formalin, the first respective reactant molar ratio is 1:0.0:0.9:1:1.84:0.62 and (e) is paraformaldehyde is 3.84 per mole of polybutyl-substituted phenol.

10. The lubricant oil composition of claim 9 wherein the normally liquid oleaginous lubricant is a mineral lubricating oil.

* * * * *