OIL-SOLUBLE ALIPHATIC ACID MODIFIED HIGH MOLECULAR WEIGHT MANNICH CONDENSATION PRODUCTS


Abstract

The thermal oxidation stability of aliphatic acid-modified high molecular weight Mannich condensation products, which are prepared by reacting (1) a high molecular weight alkyl-substituted hydroxy aromatic compound, in which the alkyl-substituent has an average molecular weight of from about 500 to about 100,000, (2) an amine compound containing at least one NH< group, (3) an aliphatic aldehyde, and (4) an aliphatic acid containing at least six carbon atoms, in the reactant molar ratio of 1.0:1--10:1--10:0.014--1.0, respectively, are improved by reacting such modified Mannich condensation products with from about 2 to about 6 moles of an aliphatic aldehyde per mole of the alkyl-substituted hydroxy aromatic compound used in preparing the modified Mannich condensation product. The products of the herein-described invention are oil-soluble, and are highly effective additives for imparting dispersant-detergent properties to lubricant oil compositions. Lubricants containing these products provide a high degree of protection against the deposition of sludge and varnish, and corrosion when used as crankcase lubricant additives.

Related Applications

This application is a continuation-in-part of our co-pending 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 new 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 depressants, 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, acide 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 (antioxidants) but also to keep in suspension (as a dispersant) and to resuspend (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, amines, imides, and amidines of polystyrene-substituted polycarboxylic acids and polymeric compounds having pendant or grafted-on polar groups. Other suggested prior additives are combinations of alkaline earth metal sulfonates and Mannich condensation products of low molecular weight alkyl (C₂₅-C₃₀) substituted hydroxyxaromatic compounds, amine having at least one replaceable hydrogen on a nitrogen and aldehydes; and alkaline 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 hydroxyxaromatic compounds having a relatively low molecular weight alkyl substituent, i.e., 2 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; 2,363,134; 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 addition 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 C₂₅-C₃₀ alkyl-substituted phenol and other hydroxy aromatic compounds, and N,N-di-substituted amine and formaldehyde.

The prior C₂₅-C₃₀ alkyl-substituted Mannich condensation products commonly are prepared by the conventional technique of adding the aliphatic aldehyde to a heated mixture of the alkylhydroxyxaromatic and amine reagents, in the presence or absence of a solvent, and then heating the resulting mixture of oils 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 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 alkaline 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 metalox, alkoxo metalox and even alkaline earth metal carbamate complex with hydroxy metalox 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. 3,569,972, 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 hydroxyaromatic compounds whose alkyl-substituent has a molecular weight in the range of 600–3000, (2) a compound containing at least one 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. 3,569,972 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 by-products 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 lubricating 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 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 our invention are oil-soluble high molecular aliphatic acid-modified high molecular weight Mannich condensation products, which are further treated with an aliphatic aldehyde. They can be made by condensing in the usual manner under Mannich reaction conditions at a temperature in the range of 150–325° F.

(1) An aliphatic-substituted hydroxyaromatic compound, in which the alkyl-substituent has an average molecular weight of about 600–100,000, preferably a polyalkylphenoxy whose polyalkyl substituent is derived from 1-monooledin polymers having an average molecular weight of about 800–2500;

(2) An amine containing at least one NH group, preferably an alkylen polyamine of the formula

$$\text{NH}_2\left(-\text{A-N}_2\right)\text{H}_n$$

wherein A is a divalent alkylen radical having 2 to 6 carbon atoms, and n is an integer from 1 to 10;

(3) An aliphatic aldehyde, preferably formaldelyde or paraformaldehyde; followed by reaction with;

(4) A 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 Mannich reaction conditions.

The above resultant modified Mannich condensation product is 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 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. Suitable condensation procedure involves adding at a temperature of from room temperature to about 200° F, the aldehyde reactant (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.

To those skilled in the art, it will be recognized that, in general, the reaction under Mannich condensation 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% in formulated crankcase lubricating oil compositions. Higher concentrations, e.g., 10% to about 70%, are useful concentrates for the manufacture of such lubricating oil compositions.

**EMBODIMENT OF THE INVENTION**

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.
3,787,458

(1) High molecular weight alkyl-substituted Hydroxyaromatics

Representative of these high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylphenol and other polyalkylyphenols. These polyalkylyphenols may be obtained by the alkylation, in the presence of an alkylation catalyst, such as BF₃, of phenol with high molecular weight polypropylene, polyethylene 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, now abandoned.

The 600 Mₙ and higher Mₙ alkyl-substituents on the hydroxyaromatic compounds may be derived from high molecular weight polypropylene, polibutenes 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%, 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%, by weight, of propylene and butene units, respectively. Said monomers copolymerizable with propylene or said butenes include but not limited to chloro, bromo, keto, ether, aldehyde, which do appreciably lower the oil-solubility of the polymer. The co-monomers polymerized with propylene or said butenes may be alkylated and can also contain non-alkylated groups, e.g., styrene, maleic anhydride, divinyl benzene and the like. From the foregoing limitation 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 alky hydrocarbon substituents having Mₙ upward from 600.

In addition to these high molecular weight hydroxyaromatic compounds other 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, xylene, hydroxy diphenyl, benzylphenol, phenethylphenol, naphthol, tolylnaphthol, among others. Preferred for the preparation of the afore-mentioned preferred bis Mannich condensation products are the polyalkylyphenol reactants, e.g., polypropylyphenol and polybutylphenol whose alkyl group has an average number molecular weight of 600–3000, 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 alkyly polyamines, principally polyethylene polyamines. Other representative monomers are copolymers containing at least 90%, 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%, by weight, of propylene and butene units, respectively. Aldehyde containing hydroxyaromatic reactants containing aliphatic hydrocarbon substituents have an HN< group suitable for use in the preparation of Mannich condensation products are well known and include the mono- and di-amino amines and their substituted analogs, e.g., ethylene diamine and diethanol amine; aromatic diamines, e.g., phenylene diamine, diamino naphthalene; heterocyclic amines, e.g., morpholine, pyrrole, pyridine, imidazole, imidazoline, and piperidine; melamine and their substituted analogs.

Suitable alkylene polyamine reactants include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentamethylene hexamine, hexamethylene heptaamino, octamethylene octammine, nonamethylene nonamine, nonylmethylenedecamine and decaethylene undecamine and mixture of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula H₂N—(A—NH—)ₓ—H, mentioned before, A is divalent ethylene and x is 1 to 10 of the foregoing formula. Corresponding polypropylene polyamines such as propylene diamine and di-, tri-, tetra-, penta-propylene tri-, tetra-, penta- and hexa-amines are also suitable reactants. The alkylene polyamines are usually obtained by the reaction of ammonia and dihalo 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 2 to 6 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 aldol (β-hydroxybutyaldehyde). 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 alkanoic (saturated) and alkenoic (mono-unsaturated) acids. The upper limit of the carbon content is restricted because of the limitation on 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 these 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 wherein 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, linoleic acid and linolenic acid and other unsaturated acids; and from oxidation or other reactions of polypropenes and polybutenes (e.g., polyisobutenes) which introduce one or more carboxylic acid group on the polymer chain.

It may be expected that the high molecular weight Mannich product modified by an unsaturated aliphatic carboxylic acid such as oleic acid or its C₁₈ saturated 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 polybutylphenol hydroxybenzyl-substituted tetraethylene pentamine containing a number average molecular weight of 3600) and the same Mannich product modified with 0.125 mole (0.8 weight percent) of each of oleic acid, isostearic acid, a mixture of C₁₀ and C₁₄ monounsaturated alkenoic acids and a mixture of C₁₂ and C₁₆ saturated alkanolic 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>Pentane insolubs, gms.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mannich product</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>Oleylic acid</td>
</tr>
<tr>
<td></td>
<td>Isostearic acid</td>
</tr>
<tr>
<td></td>
<td>Ester oil mixtures of monounsaturated acids</td>
</tr>
<tr>
<td></td>
<td>C₁₀-C₁₄ mixture of saturated acids</td>
</tr>
</tbody>
</table>
Suitable alkanoic acids having 6 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 esterification. Such suitable alkanoic acids, i.e., having R groups of 6 to 30 carbon atoms, include caproic acid, caprylic acid, capric acid, benzoic acid, lauric acid, tridecic acid, myristic acid, pentadecic acid, palmitic acid, margaric acid, stearic acid, nonadecic acid, arachidic acid, undecylid acid, behenic acid, lignoceric acid, pelargonic acid, hexadecic acid, heptadecic acid, monocosenic acid, montanic acid, and melissic acid. Many of said alkanoic acids are obtained first in mixtures of two, three or more alkanoic acids of different carbon contents from said glycerides and wax esters; said mixtures can be used in this invention in place of a single alkanoic acid reactant. When said mixtures of alkanoic 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 alkanoic 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 these 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 1600 average molecular weight polybutyl-substituted phenol (47% polybutylphenol, 53% polybutene and dioluent oil), 765 grams of a solvent-extracted 5W mineral oil, 109 grams (0.56 mole) tetraethylenetetramine, and 109 grams (0.38 mole) of a modified saturated C12-C14 fatty acid, identified as "Economy 860 Fat." After being mixed, the mixture was admixed and heated to 150° F. 84 ccs. (1.12 moles) of formalin were then rapidly added to the mixture. Thereafter, there were slowly added 168 ccs. (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 (c.f.h.). At the end of three hours the reaction mass was filtered. The recovered filtrate was clear, had a nitrogen content of 1.39%, and a SSU viscosity at 210° F. of 9.54.

**EXAMPLE II**

Part A.—2370 grams (0.73 mole) of a 1526 average molecular weight polybutyl-substituted phenol (49.4% polybutylphenol, 50.6% polybutene and oil), 300 grams of a solvent-extracted 5W mineral oil, 128 grams (0.454 mole) of tetraethylene pentamidine, and 27 grams (0.172 moles) of formaldehyde were admixed at 150° F., and 100 ccs. (1.344 moles) formaldehyde added. The temperature was increased to 300-320° F. while blowing with nitrogen at 2 c.f.h., and maintained at such temperature for 2 hours. 467 grams-extracted 5W mineral oil were added to the reaction product.

Part B.—To 3200 grams of an oleic acid-modified Mannich condensation product 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 c.f.h. 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 1028. 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 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, 6 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 prefect 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>Unmodified Mannich condensation product</th>
<th>Overbased sulfate</th>
<th>Zinc dialkyl dithiophosphate</th>
<th>Solvent-extracted 10W mineral oil</th>
<th>Solvent-extracted 5W mineral oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>4.1</td>
<td>2.0</td>
<td>1.1</td>
<td>70.0</td>
<td>22.8</td>
</tr>
</tbody>
</table>

Sample B.—Same as sample A, except that 4.1% of the product of Example II, part A, above, was used. This is an acid-modified Mannich condensation product.

Sample C.—Same as sample A, except that 4.1% of the product of Example II, part B, above, was used. This is the aldehyde treated acid-modified Mannich condensation product of the present invention.

**TABLE I**

<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 B), exhibits better thermal oxidation stability than the (sample A) and (sample C) Mannich condensation product (sample B, C), which had a letter rating of "C." As noted hereinbefore, the products of the present invention are useful addition 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 poly-
carboxylic 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.

We claim:

1. An oil-soluble aliphatic acid-modified high molecular weight Mannich condensation product prepared by the process comprising (A) reacting at a temperature of from about 150°F. to 325°F.; (a) a high molecular weight alkyl-substituted phenol wherein the alkyl substituent has an average molecular weight of from about 600 to about 100,000; (b) an alkylene polyamine; (c) formaldehyde; and (d) a higher aliphatic acid containing 10 to 30 carbon atoms, said reactants (a), (b), (c), and (d) being used in the molar ratios of 1.0:0.1–10:1.0–10:0.014–1.0, respectively, (B) then slowly adding to the resultant foregoing product of (A) at a temperature in the range of 180–300°F.; (e) additional formaldehyde in the molar ratio of from about 2 to about 6 moles thereof per mole of said reactant (a), and (C) increasing the temperature of the resultant reaction mass to from about 275°F. to about 375°F., while blowing with an inert stripping gas to dehydrate the resultant product.

2. The oil-soluble aliphatic acid-modified high molecular weight Mannich condensation product of claim 1 wherein the high molecular weight alkyl-substituted hydroxarylomatic compound is a polyalkyl-substituted phenol, wherein the polyalkyl-substituted has a molecular weight of from about 600 to about 3,000.

3. The oil-soluble aliphatic acid-modified high molecular weight Mannich condensation product of claim 2 wherein the alkylene polyamine is tetraethylene pentamine.

4. The oil-soluble aliphatic acid-modified high molecular weight Mannich condensation product of claim 2 wherein the additional aldehyde (e) is paraformaldehyde.

5. The oil-soluble aliphatic acid-modified high molecular weight Mannich condensation product of claim 2, wherein the additional aldehyde is oleic acid.

6. An oil-soluble aliphatic acid modified high molecular weight Mannich condensation product prepared by the process comprising, (A) reacting at a temperature of from 150 to 325°F.; (a) a high molecular weight alkyl-substituted phenol wherein the alkyl substituent has an average molecular weight of from about 600 to about 3,000; (b) an alkylene polyamine; (c) formaldehyde; and (d) a higher aliphatic acid containing 10 to 30 carbon atoms, said reactants (a), (b), (c), and (d) being used in the molar ratios of 1.0:1.0–10:1.0–10:0.014–1.0, respectively, (B) then slowly adding to the resultant foregoing product of (A) at a temperature in the range of 180–300°F.; (e) additional formaldehyde in the molar ratio of from about 2 to about 6 moles thereof per mole of said reactant (a), and (C) increasing the temperature of the resultant reaction mass to from about 275°F. to about 375°F., while blowing with an inert stripping gas to dehydrate the resultant product.

7. The oil-soluble aliphatic acid modified Mannich condensation product of claim 6 wherein the alkyl-substituted phenol (a) is selected from the group consisting of polypropylphenol and a polybutylphenol in which the polypropyl and polybutyl substituents have average molecular weight of from about 600 to about 3,000, the amine reactant (b) has the formula

\[ H_2 \left( \text{NH} - C(H_2)_x \right) \text{NH}_2 \]

wherein \( x \) is an integer from 1 to 10, aldehyde (c) is formalin, the aliphatic acid (d) is a fatty acid having from about 10 to about 20 total carbon atoms per carboxylic acid group, and the additional aldehyde (e) is paraformaldehyde.

8. The oil-soluble aliphatic acid modified high molecular weight Mannich condensation product of claim 6 wherein the alkyl-substituted phenol is a polypropylphenol (a) in which the polypropyl substituent has an average molecular weight of about 1,500, the alkylene polyamine (b) is tetraethylene pentamine, aldehyde (c) is formalin, the aliphatic acid (d) is oleic acid, and the additional aldehyde (e) is paraformaldehyde.

9. A method of preparing the oil-soluble acid-modified high molecular weight Mannich product of claim 1 as solute in the presence of hydrocarbon diluent consisting essentially of aliphatic hydrocarbon of 600–100,000 average molecular weight and mineral lubricating oil which comprises reacting at a temperature in the range of 150–325°F. and in the presence of said diluent said reactants (a), (b), (c), and (d) in the respective molar ratio of 1.0:1.0–10:1.0–10:0.014–1.0 and then further reacting (e) 2–6 moles additional of formaldehyde per mole of reactant (a) at a temperature in the range of 275–375°F. while blowing with inert stripping gas until the resultant product is dehydrated, wherein the amount of said diluent used provides 10–70 weight percent of said Mannich product as solute.

10. The method of claim 9 wherein the hydrocarbon diluent is butene polymer derived hydrocarbon of about 1500 number average molecular weight and SAE-5W oil, reactant (a) is about 1500 number average molecular weight polypropyl-substituted phenol, (b) is tetraethylene pentamine, (c) is formaldehyde, (d) is oleic acid and (e) is paraformaldehyde and wherein the amount of said diluent provides 40 weight percent of said Mannich product as solute.

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GLENNON H. HOLLRAH, Primary Examiner

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252—51.5, 51.5 A; 260—247.7, 249.6, 293.89, 293.9, 309, 309.7, 326.5, 326.8, 404, 561 R, 561 N, 562 R, 562 P
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,787,458 Dated January 22, 1974

Inventor(s) Edmund J. Piasek and Robert E. Karll

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, Line 49 - bis Mannich should be bis-Mannich
Column 8, Line 4 - c.f.h. should be C.F.H.
Column 8, Line 47 - c.f.h. should be C.F.H.
Column 9, Line 27 - 0 should be 1.0

Signed and sealed this 29th day of October 1974.

(SEAL)

Attest:

McCoy M. Gibson Jr. C. Marshall Dann
Attesting Officer Commissioner of Patents