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Piasek et al.

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[54] OIL SOLUTION OF ALIPHATIC ACID DERIVATIVES OF HIGH MOLECULAR WEIGHT MANNICH CONDENSATION PRODUCT

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Related U.S. Application Data

[62] Division of Ser. No. 54,558, July 13, 1970, Pat. No. 3,641,799.

[52] U.S. Cl..... 252/51.5 A

[51] Int. Cl..... C10m 1/32

[58] Field of Search..... 252/51.5 A

[56] References Cited

UNITED STATES PATENTS

3,493,520 2/1970 Verdol et al..... 252/51.5 A

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[57] ABSTRACT

Protection against corrosion and deposition of sludge and varnish is provided by lubricating oils containing a minor amount of the ashless addition agents which are aliphatic acid derivatives of high molecular weight Mannich condensation products of (1) high molecular weight alkyl-substituted hydroxy aromatic compounds whose alkyl-substituent has a number average molecular weight (M_n) from about 600–100,000, (2) a compound containing at least one

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group, (3) an aldehyde in the respective molar reactant ratio of 1:0.1–10:1.0–10, and (4) 0.1–10.0 weight percent of an aliphatic acid having at least 6 carbon atoms.

10 Claims, No Drawings

**OIL SOLUTION OF ALIPHATIC ACID
DERIVATIVES OF HIGH MOLECULAR WEIGHT
MANNICH CONDENSATION PRODUCT**

RELATED APPLICATION

This application is a division of copending application Ser. No. 54,558, filed July 13, 1970 which is now U.S. Pat. No. 3,641,799.

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 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 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.

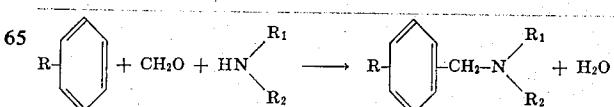
Various ingredients have been developed for the purpose of providing the dispersant-detergent function.

Neutral and overbased metallo-organic compounds, such as the alkaline earth metal salts of sulfonic acids and hydrocarbon-P₂S₅ reaction products were the first addition agents used for this purpose. Their in-service drawbacks included the formation of metal-ash thermal decomposition products which deposited on engine parts; they could not efficiently disperse or resuspend lacquer or varnish formers or sludge formers; and they lost their dispersant-detergent function when their alkaline earth metal component had been consumed in neutralizing acidic products of combustion.

As performance levels increased and the recommended periods between oil drains lengthened for both automobile and railway Diesel engines, more efficient dispersancy and detergency performance as well as acid neutralization and lower ash-forming tendency were demanded for lubricating oil formulations. During the past several years, a great deal of time and effort has been directed at providing addition agents for lubricants capable of satisfying such performance demands. When high molecular weight polybutene polymers became commercially available in the early 1940's, research workers in various laboratories devised, for this dispersant-detergent function, a series of derivatives of polybutene-phosphorus pentasulfide reaction products, e.g. alkaline earth metal salts, alkylene polyamine and alkylene oxide derivatives, in which the high molecular weight of the polybutene group greatly enhanced their effectiveness. Others devised amine salts, amides, imides and amidines of polybutenyl-substituted polycarboxylic acids and polymeric compounds having pendant or grafted-on polar groups. Still others suggested combinations of alkaline earth metal sulfonates and Mannich condensation products of a low molecular weight alkyl (C₂-C₂₀) substituted hydroxyaromatic compound, an amine having at least one replaceable hydrogen on a nitrogen and an aldehyde and alkaline earth metal salts (phenates) of those Mannich condensation products but without notable success. The later compositions still possessed the objectionable feature of forming harmful metal-ash deposits, and were incapable of providing the increased dispersancy-detergency service demanded for long drain service of present-day engine requirements.

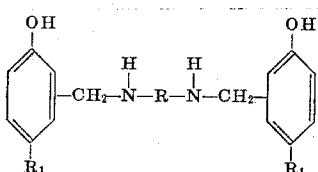
Mannich condensation products derived from alkyl-substituted hydroxyaromatic compounds having a relatively low molecular weight alkyl substituent, i.e., 2 to 20 carbon atoms in the alkyl substituent and chlorinated wax (straight chain) type alkyl-substituents are described in U.S. Pat. Nos. 2,403,453; 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 C₂-C₂₀ alkyl-substituted phenol and other hydroxy aromatic compounds, and N,N-di-substituted amine and formaldehyde according to the following equation:



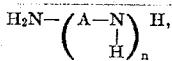
wherein R is an alkyl group having between 2 and 20 carbon atoms and R₁ and R₂ may be alkyl, cycloalkyl, aryl or arakyl radicals.

Other prior low molecular weight Mannich condensation products formed by condensing a C₂ to C₂₀ alkyl-substituted phenol, an alkylene diamine and an aldehyde in the respective molar ratios of 2:1:2, have been illustrated by the following structural formula:



wherein R is a divalent alkylene hydrocarbon radical and R₁ is an alkyl group containing from 2 to 20 carbon atoms.

Still others have been prepared by reacting C₂-C₂₀ alkylphenols, formaldehyde and alkylene polyamines of the formula



wherein A is a divalent alkylene radical of 2 to 6 carbon atoms and n is an integer from 1 to 10, in the ratio of from 0.5 to 2 moles each of C₂-C₂₀ alkylphenol and formaldehyde for each nitrogen group contained in the alkylene polyamine reagent. The molar reactant ratio range of C₂-C₂₀ alkylphenol, amine and formaldehyde used to form such products is 1-20:1.0:1-20. U.S. Pat. No. 3,036,003 exemplifies such products, which usually are formed with ethylene polyamines, according to the above formula in which A is -CH₂-CH₂- and n is 2, 3 and 4.

The foregoing prior C₂-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 are light minerals 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 exactly 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 exactly 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. 3,235,484 issued Feb. 15, 1966 (Now U.S. Pat. Reissue No. 26,330) describes the addition agents of certain disclosed compositions to refinery hydrocarbon feed stocks for the purpose of inhibiting the accumulation of carbonaceous deposits in refinery cracking units. The primary inhibitors disclosed are mixtures of amides, imides and amine salt formed by reacting an ethylene polyamine with hydrocarbon sub-

stituted succinic acids or anhydride, whose hydrocarbon substituent has at least about 50 carbon atoms. As an adjunct for such primary carbonaceous deposit inhibitors there is disclosed in said patent Mannich condensation products formed by reacting (1) alkylphenol,

(2) an amine and (3) formaldehyde in the ratio of one mole alkylphenol and from 0.1-10 mole formaldehyde for each active nitrogen group contained in the amine reactant. Alkylphenols whose alkyl group has a molecular weight as high as 50,000 and contains from mo-

noalkylphenols whose alkyl group contains 4-30 carbon atoms are stated to be the preferred alkylphenol reactants.

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 hydroxyaromatic compounds whose alkyl-substituent has a molecular weight in the range of 600-3,000, (2) a compound containing at least one

HN³⁵ group and (3) an aldehyde in the respective molar ratio of 1.0:0.1-10:1.0-10.

Said high molecular weight Mannich condensation products of either U.S. Pat. No. 3,235,484 or 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 borderline soluble by-products which not only are not only 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.

We have discovered that both of those drawbacks can be overcome by the use of an aliphatic acid having suitably from about 6 carbon atoms to about 30 carbon atoms, desirably at least 10 carbon atoms and preferably 16 or more carbon atoms per carboxylic acid group. The aliphatic acid can be used as an initial reactant, reacted with the hazy high molecular weight Mannich condensation product before its filtration or added to the filtered product before it goes to storage. Such uses of the aliphatic acid require only small amounts, in the

range of 0.1-10.0 weight percent to eliminate those drawbacks and provide an improved product.

BRIEF SUMMARY OF THE INVENTION

This invention pertains to lubricant oil compositions comprising a major amount of lubricating oil and a minor amount, 0.05 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.

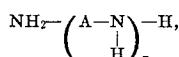
The new class of compounds which comprise the addition agent component of this invention are oil-soluble high molecular aliphatic acid modified weight products of the Mannich Reaction. They can be prepared either by condensing in the usual manner under conditions of the Mannich Reaction:

1. an alkyl-substituted hydroxyaromatic compound, whose alkyl-substituent has a 600-100,000 Mn, preferably a polyalkylphenol whose polyalkyl substituent is derived from 1-mono-olefin polymers having a Mn of about 850-2,500;

2. an amine containing at least one



group, preferably an alkylene polyamine of the formula



wherein A is a divalent alkylene radical having 2 to 6 carbon atoms and x is an integer from 1 to 10; and

3. an aldehyde, preferably formaldehyde followed by reaction with (4) 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 foregoing high molecular weight products of this invention are preferably prepared according to the conventional methods heretofore employed for the preparation of Mannich Reaction condensation products, using the above-named reactants in the respective molar ratios of high molecular weight alkyl-substituted hydroxyaromatic compound, amine, aldehyde and aliphatic acid of approximately 1.0:0.1-10:1.0-10:0.0-14-1.0. Suitable as a condensation procedure involves adding at a temperature of from room temperatures to about 200° F. the formaldehyde reagent (e.g. formalin) to a mixture of reagents (1), (2) and (4) above or in an easily removed organic solvent, such as benzene, xylene or toluene or in solvent refined neutral oil and then heating the reaction at an elevated temperature (275°-375° F.) preferably flowing 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 Mn polyalkylphenol; (2) an ethylene polyamine, as amine reactant; (3) formaldehyde and (4) an aliphatic acid in the respective molar ratio of 1.0:0.7-1.0:1.5-2.1:0.0-14-0.62.

The novel addition agents according to our invention are the high molecular weight aliphatic acid modified Mannich Reaction condensation products of (1) high molecular weight alkyl-substituted phenol whose alkyl

substituent has a Mn of 600-100,000, a compound having at least one



group, an aldehyde and an aliphatic acid wherein the respective molar ratio of the reactants is 1.0:0.1-10:1-10:0.014-0.62. Preferred addition agents are those obtained by condensing (1) an alkylphenol whose alkyl substituent is derived from 1-mono-olefin polymers having a 850-2,500 Mn; (2) an alkylene polyamine having the formula $\text{H}_2\text{N}-(\text{A}-\text{NH})_n\text{H}$ wherein A is a divalent saturated hydrocarbon radical having 2 to 6 carbon atoms and n is an integer from 1 to 10, (3) a formaldehyde yielding reactant and (4) an aliphatic acid having 10-20 carbon atoms per carboxylic acid group used in the respective molar ratio of reactants is 1:0.7-1.0:1.5-2.1:0.014-0.62.

The high molecular weight products of this invention are exceptionally useful addition agents for lubricating oils imparting thereto dispersant-detergent and antioxidant properties at relatively low concentrations of the addition agent, e.g., 0.05 to 10 weight percent in formulated crankcase lubricating oil. Higher concentrations, e.g., 10 to 70 weight percent, are useful concentrates of the preparation of those formulated crankcase lubrication oils and the fortification of crankcase oil in use prior to the scheduled complete drain. For a more complete understanding of the Mannich Reaction see "Organic Reactions," Vol. 1 pages 303 to 341 (1942) published by John Wiley & Sons, Inc.

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, oily polybutene VI improver and/or the polyacrylate type VI improver.

EMBODIMENTS 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.

1. High Molecular Weight Alkyl-Substituted Hydroxyaromatics

Representative of these high molecular weight alkyl-substituted hydroxyaromatic compounds are polypropylphenol, polybutylphenol and other polyalkylphenols. These polyalkylphenols may be obtained by the alkylation, in the presence of an alkylating catalyst, such as BF_3 , 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

preparations using a BF_3 phenol catalyst is described and claimed in our copending application Ser. No. 484,758, filed Sept. 2, 1965.

The 600 M_n and higher M_n 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%, 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 monomers containing a small proportion of unreactive polar groups such as chloro, bromo, keto, ethereal, aldehyde, which do appreciably lower the oil-solubility of the polymer. The comonomers 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 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 alkyl hydrocarbon substituents having M_n 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, tolylnaphthol, among others. Preferred for the preparation of the before mentioned preferred bis Mannich condensation products are the polyalkylphenol reactants, e.g., polypropylphenol 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 850-2,500.

2. $\text{HN} \swarrow$ GROUP CONTAINING REACTANTS

Representative of this class of reactants are alkylene polyamines, principally polyethylene polyamines. Other representative organic compounds containing at least one



group 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, diamino naphthalenes; heterocyclic amines, e.g., morpholine, pyrrole, pyrrolidine, imidazole, imidazolidine, and piperidine; melamine and their substituted analogs.

Suitable alkylene polyamine reactants include ethylenediamine, diethylene triamine, triethylene tetraamine, tetraethylene pentamine, pentaethylene hexamine, hexaethylene hpta-amine, heptaethylene octa-amine, octaethylene nonamine, nonaethylene decamine

and decaethylene undecamine and mixture of such amines having nitrogen contents corresponding to the alkylene polyamines, in the formula $\text{H}_2\text{N}-(\text{A}-\text{NH}-)_n\text{H}$, mentioned before, A is divalent ethylene and n is 1 to 10 of the foregoing 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 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 (b-hydroxybutyraldehyde). We prefer to use formaldehyde or a formaldehyde yielding reactants.

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 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, euric 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 might be expected that the high molecular weight Mannich product modified by an unsaturated aliphatic carboxylic acid such as oleic acid or its C_{16} 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-, 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 C_{16} and C_{18} monounsaturated alkenoic acids and a mixture of C_{16} and C_{18} saturated alkanoic acids. The pentane insolubles content of these tests, indicative of oxidation stability, is measured and is as follows:

Additive	Acid Modifier	Pentane Insolubles - Gms.
Mannich Product	none	
do.	oleic acid	1.5
do.	isostearic acid	2.5
do.	C_{16} - C_{18} mixtures of monounsaturated acids	3.0
do.	C_{16} - C_{18} mixture of saturated acids	3.0
		2.0

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 synthesis. Such suitable alkenoic acids, i.e. having R groups of 6 to 30 carbon atoms, include caproic acid, caprylic acid, capric acid, hendecylic acid, lauric acid, tridecyclic acid, myristic acid, pentadecylic acid, palmitic acid, margaric acid, 25 stearic acid, nonadecylic acid, arachidic acid, medullic acid, behenic acid, lignoceric acid, pentacosic acid, cerotic acid, heptacosic acid, monocosic 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 alkenoic acids having a total of at least six carbon atoms include those from hexenoic, heptenoic, octenoic, etc. acids up to oleic (C_{18}) and erucic (C_{22}) 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.

At this point an explanation of various products possible within our invention is in order. In general, the reaction under Mannich condensation conditions, like other chemical reactions, does not go to theoretical completion and some portion of the reactants, generally the amine, remains unreacted or only partially reacted as a coproduct. Thus even when a portion of a mono-functional amine reactant (one having only one

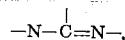
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ner before mentioned. Such enhancement is achieved with relatively small amounts of the aliphatic acid relatively small, for example in the range of 0.01 to 0.03 mole aliphatic acid per mole of high molecular weight alkyl-substituted hydroxy aromatic compound before described as reactant (1).

Pentane Insolubles - Gms.

Under conditions at which water splits out, the aliphatic acid reacts with such H_2N - and/or



groups to form an amide linkage. An imidazo:



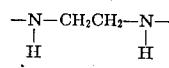
linkage is possible. For example when the aliphatic acid reacts with two H_2N - groups, or one each of H_2N - and



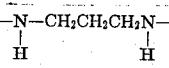
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groups are separated by two or three carbon atoms as in moiety derived from ethylene diamine, ethylene polyamines, propylene 1,2- and 1,3-diamines, propylene polyamines, 1,2- or 1,3-diaminobenzene or reacts with two molecules each having one



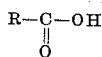
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or H_2N - group. For example, the moiety derived from an ethylene diamine (in this case from both ethylene diamine and ethylene polyamine):



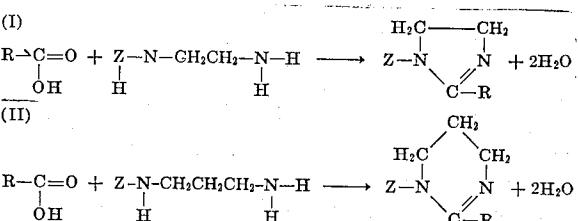
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or from a propylene diamine (likewise in this case from both propylene diamine and propylene polyamine):



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The foregoing formation of the imidazo linkage can be illustrated by the reactions of an alkanoic acid



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(e.g. stearic wherein R has 17 carbon atoms) and N-(2-hydroxy-5-polybutylbenzyl) ethylene and propylene diamines wherein Z is said 2-hydroxy-5-polybutylbenzyl group in the following equation:



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group) is used either the portion of unreacted amine or its partial reaction product (co-product) there appears to be a sufficiently reactive amine species to react with the aliphatic acid to form a stable oil soluble product that appears to enhance the total product in the man-

The cyclic product of Equation I is 1-(2-hydroxy-5-polybutylbenzyl)-2-n-heptadecylimidazoline and of Equation 2 is 1-(2-hydroxy-5-polybutylbenzyl)-2-n-heptadecyl-1,4,5,6-tetrahydropyrimidine. Such specific compounds can be present in the reaction mixture resulting from the reaction of (1) polybutylphenol, (2) ethylene diamine or 1,3-propylene diamine, (3) formaldehyde and (4) stearic acid in the respective reactant mole ratio of 1.0:1.0:1.0:1.0 but other related products can also be and are, in general, also present in admixture thereof. Mixtures of related products do generally form when the four classes of reactants (1), (2), (3) and (4) before defined are used broadly in the respective molar ratio of reactants 1.0:1.0-10:1.0-10:0.01-10.0. Hence the products of this invention cannot be properly characterized with precision by chemical structural formula but rather must be characterized as reaction products.

The following examples are illustrative of preferred embodiments of the present invention.

EXAMPLE I

There were combined, with stirring, at a temperature of 180° F., 2300 grams (0.66 mole) of a 1,600 molecular weight polybutyl substituted phenol (46% polybutyl phenol, 54% polybutene and 690 grams of a solvent-extracted 5W mineral oil) 115 grams (0.61 mole) tetraethylene pentamine, and 93 grams (0.33 mole; equivalent 0.5 mole per mole polybutyl phenol) oleic acid. Thereafter, 90 ccs. (1.2 mole) formaldehyde were slowly added, and the temperature raised to 300° F., with nitrogen bubbled through the mixture at the rate of 2 cubic feet per hour (CFH). After heating at 300° F. for 3 hours, a filter-aid, such as Celite, was added and the mixture filtered. The recovered filtrate had a nitrogen content of 1.24%, a SSU viscosity at 210° F. of 677, and was crystal clear.

EXAMPLE II

The method of Example I was repeated, except that 1,540 grams (0.444 mole) of the polybutyl phenol, 460 grams of the mineral oil, 77 (0.41 mole) grams of tetraethylene pentamine, 62 (0.220 mole; equivalent 0.5 mole per mole polybutyl phenol) grams oleic acid, and 60 ccs. (0.816 mole) formaldehyde were used. The recovered filtrate was crystal clear, contains 1.2% nitrogen and had a SSU viscosity at 210° F. of 679.

EXAMPLE III

400 grams (0.111 mole) of a 1,600 molecular weight polybutyl substituted phenol (44.5% polybutyl phenol, 55.5% polybutene and 86 grams of a solvent-extracted 5W mineral oil) 8 grams (0.028 mole; equivalent 0.25 mole per mole polybutyl phenol) oleic acid, and 19.3 grams (0.102 mole) tetraethylene pentamine were admixed at 180°F. 15 ccs. (0.204 mole) formaldehyde were then added, the temperature raised to 320° F., and maintained at said temperature for 3 hours, while introducing nitrogen at the rate of 0.5 CFH. A filter-aid was added and the product filtered. The recovered filtrate was crystal clear, contained 1.15% nitrogen, and had a SSU viscosity at 210° F. of 827.

EXAMPLE IV

A mixture of 400 grams of a polybutyl phenol, as used in Example III, 96 grams of a solvent-extracted 5W mineral oil, and 19.3 grams (0.102 mole) tetraeth-

ylene pentamine was heated to 150° F., and 15 ccs. (0.204 mole) formaldehyde added. The mixture was then heated to 220° F. and 16 grams (0.056 mole; equivalent 0.50 mole per mole polybutyl phenol) added, and the resultant mixture heated at 300°-320° F. for 3 hours while bubbling nitrogen through the reaction mixture at the rate of 0.5 CFH. At the end of 3 hours, a filter-aid was added and the mixture filtered. The recovered filtrate was crystal clear, contained 1.24% nitrogen, and had a SSU viscosity at 220° F. of 739.

EXAMPLE V

2,395 grams (0.666 mole) of a polybutyl phenol, as used in Example III, 328 grams of a solvent-extracted 5W mineral oil, 24 grams (0.084 mole; equivalent to 0.125 mole per mole of the polybutyl phenol) oleic acid, and 116 grams (0.612 mole) tetraethylene pentamine were mixed at a temperature of 180° F., and then 90 ccs. (1.21 mole) formaldehyde were added. The reaction mixture was then heated to 340°-360° F., and maintained at such temperature for 4 hours, while nitrogen at the rate of 0.5 CFH was bubbled through the reaction mixture. A filter-aid was added, and the mixture filtered. The recovered filtrate was crystal clear, contained 1.4% nitrogen, and had a SSU viscosity at 210° F. of 1070.

EXAMPLE VI

476 grams (0.132 mole) of a polybutyl phenol, as used in Example III, 84 grams of a solvent-extracted 5W mineral oil, 19 grams (0.066 mole; equivalent to 0.5 mole per mole of the polybutyl phenol) stearic acid, and 23 grams (0.122 mole) tetraethylene pentamine were admixed at 180° F., and then 18 ccs. (0.24 mole) formaldehyde added. The reaction mixture was then heated to 300° F. and reacted at said temperature for 3 hours, while nitrogen at the rate of 0.5 CFH. Filter-aid was then added and the mixture filtered. The recovered filtrate was clear, contained 1.22% nitrogen and had a SSU viscosity at 210° F. of 957.

EXAMPLE VII

238 grams (0.066 mole) of a polybutyl phenol, as used in Example III, 37 grams of a solvent extracted 5W mineral oil, 5.7 grams (0.033 mole; equivalent to 0.5 mole per mole of the polybutyl phenol) capric acid, and 11.5 grams (0.061 mole) tetraethylene pentamine were mixed at 180° F., and then 9.0 ccs. (0.12 mole) formaldehyde added. The reaction temperature was raised to 300° F. and maintained at said temperature for 3 hours while blowing with nitrogen at the rate of 0.5 CFH. Filter-aid was added, and the reaction mass filtered. The recovered filtrate was crystal clear, contained 1.48% nitrogen, and had a SSU viscosity at 210° F. of 978.

EXAMPLE VIII

Same procedure as used in Example VII, but using 7.5 grams (0.033 mole; equivalent to 0.5 mole per mole of the polybutyl phenol) myristic acid (in place of capric acid) and 40 grams of the mineral oil. The recovered filtrate was crystal clear, contained 1.4% nitrogen, and had a SSU viscosity at 210° F. of 967.

EXAMPLE IX

Same procedure as used in Example VII, but using

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8.5 grams (0.033 mole; equivalent to 0.5 mole per mole of the polybutyl phenol) palmitic acid (in place of capric acid), and 41 grams of the mineral oil. The recovered filtrate was crystal clear, had a nitrogen content of 1.32%, and had a SSU viscosity at 210° F. of 975.

EXAMPLE X

476 grams of a polybutyl phenol, as used in Example III, 84 grams of a solvent-extracted mineral oil, 18.6 grams (equivalent to 0.5 mole per mole of the polybutyl phenol) of a mixture of fatty acids, consisting principally of C_{16} and C_{18} monobasic acids, marked as "Emery 894" by Emery Industries, Inc., and 23 grams of tetraethylene pentamine were mixed together and heated to 170° F. Eighteen cubic centimeters formaldehyde were then added and the mixture heated to 300°-320° F., and blown with nitrogen at the rate of 0.5 CFH for 2 hours. A filter-aid was added and the mixture filtered. The recovered filtrate was crystal clear, and had an SSU viscosity at 210° F. of 967.

The resistance to haze formation exhibited by the fatty acid modified high molecular weight Mannich condensation products of the present invention is demonstrated by the data in Table I below. In this storage stability test the samples are stored at 160° F. for 14 days and then observed for their clarity.

TABLE I

Sample	Acid	Moles*	Clarity**		
			Initial	14 Days	160°F.
Example I	Oleic	0.5	7		7
Example VI	Stearic	0.5	7		7
Example VII	Capric	0.5	7		7
Example VIII	Myristic	0.5	7		7
Example IX	Palmitic	0.5	7		7
Example X	"Emery 894"	0.5	7		7
Control***	—		7		5

* Moles of acid per mole of the polybutyl phenol.

** 7 indicates crystal clear; 5 indicates barely transparent

*** High molecular weight Mannich condensation product prepared without fatty acid modifier

A lubricating oil composition containing a fatty acid modified high molecular weight Mannich condensation

measured and percent filling determined. The extent of varnish lacquer deposit on piston lands and in the lower grooves is evaluated. To qualify, a lubricating oil formulation test should result in no more than, and desirably, less than 30% carbon deposit in the top ring groove. Varnish is the second groove and on the first land should not exceed 50%. Below this the piston must be clean.

The following oil formulation was used in the Caterpillar 1-H Test:

Solvent-extracted SAE5 Oil	23.03% (Vol.)
Solvent-extracted SAE10 Oil	70.00% do.
Fatty acid modified product of Example I	4.00% do.
Magnesium Sulfonate	1.00% do.
Zinc dialkyl dithiophosphate	0.88% do.
Pour-point Depressor*	0.50% do.
Silicone Polymer Anti-foam Agent	5 ppm
*Wax alkylated naphthalene	

The results of the "Caterpillar 1-H Test" using the above formulation is shown in the following Table II.

20 For comparison, values obtained with a lubricating oil composition containing an unmodified high molecular weight Mannich condensation product are indicated in parentheses. The formulation of this oil composition was as follows:

25 Mineral lubricating oil base 94.5% (Vol.)
 Unmodified high molecular weight 3.5% do.
 Mannich condensation product

TABLE II

Grooves		240 Hours
1	Top groove fill-2% (5%)	Top groove fill-8% (44%)
2	Clean (27%)	Clean (22%)
3	Clean (Clean)	Clean (Clean)
4	Clean (Clean)	Clean (Clean)
Lands		
1	Clean (12% AL*, LAL 14%)	Clean (2% BIL, 21% AL, 17% LAL, 60% Clean)
2	Clean	Clean
3	Clean	Clean
Undercrown Deposits		
	50% Light-Very light	25% Light Amber Lacquer
	Amber Lacquer	25% Medium Amber Lacquer
		Pass (Fail)

* AL-Amber Lacquer
LA-L-Light Amber Lacquer
BL-Black Lacquer

product of the present invention was submitted to the Caterpiller 1-H Test. This test, a 480 hour test, conducted with a high-speed, super-charged Caterpillar diesel engine, is designed to measure the high temperature detergency properties of a crankcase lubricating oil for qualification under Army Ordnance Specification M1.L-2104B. The performance of a candidate lubricating oil formulation is determined by inspection of piston top ring grooves for carbon deposit which is

65 Another lubricating oil composition containing the fatty acid modified high molecular weight Mannich condensation product described in Example II, supra, was tested in the so-called "289 Ford Test." This test, made in a Ford 289 cubic inch displacement engine, is conducted in the same manner as the so-called "Lincoln MS V Test Sequence," described in U.S. Pat. No. 3,442,808, except for the apparent difference in the test engines. The "289 Ford Test" is more severe with

respect to both sludge and varnish formation and deposition since the test is conducted with vapors from the crankcase being introduced into the engine fuel intake system by means of a positive crankcase ventilation system.

The following oil formulation was used in the "289 Ford Test":

Solvent-extracted 5W Oil	37.15% (Vol.)
Solvent-extracted 10W Oil	47.00% do.
Polybutene V.I. Improver	2.80% do.
Acryloid V.I. Improver & Pour-point Agent	4.95% do.
Fatty acid modified product of Example II	5.00% (Vol.)
Zinc dialkyl dithiophosphate	1.10% do.
Magnesium Sulfonate	2.00% do.

The result of the "289 Ford Test" using the above formulation is shown in the following Table III. For comparison, the values obtained with a lubricating oil composition containing an unmodified high molecular weight Mannich condensation product are indicated in parentheses. The formulation of this oil composition was as follows:

Solvent-extracted 20 Oil	93.22% (Vol.)
Unmodified high molecular weight Mannich condensation product	5.00% do.
Zinc dialkyl dithiophosphate	0.78% do.
Magnesium Sulfonate	1.00% do.

Table III

Varnish		Sludge	
Piston Varnish	8.5 (8.2)	Rocker Arm Cover	9.8 (7.5)
Rocker Arm Cover	9.0 (9.0)	Intake Manifold	9.8 (8.0)
Lifter Body	6.0	Oil Screen	10.0 (10)
Cylinder Walls	8.9 (6.8)	Oil Pan	9.8 (7.3)
Oil Pan	9.8 (9.4)	Valve Deck	9.8 (7.7)
Total Varnish	42.2 (39.2)	Push Rod Chamber	9.8 (7.8)
Oil Pump Relief Valve	9.8 (9.3)	Timing Gear Cover	9.8 (7.7)
Lifter Deposits, Plunger		Total Sludge	49.1 (39.5)
		Plugging of Oil Rings	None (none)
		Piston Ring Sticking	None (none)
		Oil Consumption (Qts.)	5.35 (5.22)
		Intake Valve Tip Wear	
Varnish	Clean (Clean)	Max. 0.0027 (0.0013)	
Rust	9.8 (9.8)	Avg. 0.0012 (0.0010)	
Lifter Sticking	None (None)	Min. 0.0005	
Plugging of Oil Screen	None (None)		
Push Rod Plugging	None (None)		
Blowby, CFH:			
Max. 158			
Avg. 152			
Min. 146			
Intake Valve Tulip Deposits 7.5			

In the above test the engine components are examined visually and rated on a scale of 1 to 10, a value of 10 being a perfect rating indicating no sludge or varnish. A rating of 50 for total sludge and for total varnish is considered perfect; a rating of 60 or lower is considered passing for screen plugging; and a rating of 50 or lower is considered passing for ring plugging. From the data in Table III it is evident that the fatty acid modified high molecular weight Mannich condensation products of the present invention are more effective than the unmodified products, and are free of the haze drawbacks.

As noted hereinbefore the products of the present invention are useful addition agents for lubricating oils. Such lubricating oils can be any normally liquid oleaginous lubricant, such as hydrocarbon oils, both natural, i.e., petroleum oils, and synthetic oils, for example,

those obtained by the polymerization of olefins, as well as synthetic lubricating oils of the alkylene oxide type, and the polycarboxylic acid ester type, such as the oil-soluble esters of adipic acid, sebacic acid, azelaic acid, 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 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:

15 1. A lubricant oil composition comprising a major amount of a normally liquid oleaginous lubricant and a minor detergent-dispersant amount of an oil-soluble aliphatic acid modified high molecular weight product of the Mannich Reaction conducted at a temperature

20 of from about 300° F. to about 375° F., with:
a. a high molecular weight alkyl-substituted hydroxyaromatic compound wherein the alkyl substituent has an average molecular weight of from about 600 to about 100,000;

25 b. an amine containing at least one



group;

c. an aliphatic aldehyde; and

HN_n

group;

c. an aliphatic aldehyde; and

5. The lubricant oil composition of claim 2, wherein the amine is selected from the group consisting of tetraethylene pentamine and diethylene triamine.

6. The lubricant oil composition of claim 2, wherein the aldehyde is selected from the group consisting of formaldehyde and 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 reactants are:

a. polybutyl-substituted phenol in which the polybutyl-substituent has an average molecular weight of from about 600 to about 3,000;

b. ethylene polyamine;

c. formaldehyde affording reactant; and
d. oleic acid and wherein said reactants are used in the respective reactant molar ratio of 1:0.7-1.0:1.5-2, 1:0.014-1.0.

5 9. The lubricant oil composition of claim 8 wherein the polybutyl-substituent has a molecular weight of about 1,500, the ethylene polyamine is tetraethylene pentamine and the formaldehyde affording reactant is formaldehyde.

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

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