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LUBE OIL DISPERSANTS

Thornton P. Traise, Chicago Heights, and Edmund J. Piasek, Chicago, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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ABSTRACT OF THE DISCLOSURE

Modified Mannich type condensation products from a polymer substituted phenol, an alkylene polyamine and formaldehyde wherein a portion of the alkylene polyamine is replaced with an alkyl-substituted pyridine. These products are useful as lubricating oil dispersants.

Background of the invention

This invention relates to modified Mannich condensation products as novel compounds and more particularly relates to novel condensation products C_{50} and higher alkyl-substituted phenols, formaldehyde, alkylene polyamine, and an alkyl-substituted pyridine; their preparation and their use as detergent-dispersant addition agents for lubricant oil formulations.

The prior art portrays a need for improved engine lubricating oil additives which function as dispersants to retain in suspension insoluble particles such as the products of fuel combustion, those of incipient oxidation, and those of lubricant deterioration. The control of the deterioration of lubricating oils has long been a problem, particularly in the formulation of the compositions of lubricating oil additives.

It has been known for many years that deterioration of hydrocarbon lubricating oils causes the formation of substances which deleteriously affect the surfaces which the lubricants are developed to protect through the maintenance of reduced frictional forces between said surfaces. Lubricating oil deterioration not only causes the formation of surface-deleterious substances, but it also results in the agglomeration of sludge-like materials in the lubricants and the deposition of varnish on the surfaces.

For many years it has been a practice to include as additives in lubricating oils, chemical compositions which tend to reduce oil deterioration and the consequent formation of the sludge- and varnish-like material. Broadly included in the classification of additives are corrosion and oxidation inhibitors, and dispersing agents. These additives generally function to reduce the corrosion of the surfaces to be protected, to stabilize the lubricating oil, to inhibit deterioration by oxidation, and to function as dispersants which tend to prevent the agglomeration of sludge and the deposition of varnish and sludge caused by the formation of the products of deterioration.

Frequently, the inclusion into lubricating oils of corrosion, oxidation, and dispersant agents is highly desirable; however, the problems of compatibility of these three or more functional agents creates serious difficulties in the formulation of useful additive-containing lubricating oils. Much research and development effort has been expended in the search for improved lubricating oil additives which function in the above-enumerated manner. The research efforts have been directed toward the development of three or more separate agents, as well as a single agent, or a plurality of compatible agents that will perform all of the desired functions when incorporated into hydrocarbon lubricating oils.

Various Mannich condensation products are known in the prior art as lubricating oil additives; however, the teachings of the disclosures indicate that these Mannich products have previously been considered for use as oxidation inhibitors and as anti-wear additives. The former tend to reduce the rate of formation of oxidation products and the latter tend to coat surfaces with films and reduce friction resulting in less wear; consequently, there is some reduction of particulate and product contamination of the lubricating oil medium. It is also well-known that various Mannich products produced for use as oxidation inhibitors and anti-wear additives demonstrate limited solubility in lubricating oil, which factor is also an undesirable characteristic of an additive. In view of the above, it has long been attempted to develop Mannich products and derivatives thereof which have novel functional properties as well as improved solubility in lubricating oils when incorporated therein.

Accordingly, it is an object of this invention to provide new compositions of matter.

It is an additional object of this invention to provide new compositions of matter which are useful as dispersants in lubricating oil compositions.

Another object of this invention is to provide lubricating oil dispersants which have improved solubility in said oil and which exhibit superior compatibility with other oil including additives.

An additional object of this invention is to provide a novel process for the preparation of compositions useful as dispersants.

Another object of this invention is to provide improved lubricating compositions.

Other objects and advantages of the invention disclosed and claimed herein will become apparent from the specification, including various embodiments, examples, and the claims.

Summary of the invention

It has been discovered that improved dispersant-detergent compositions for lubrication oils can be made by condensing a phenol substituted with a high molecular weight hydrocarbon with an aldehyde, an alkylene polyamine, and an alkyl-substituted pyridine. Suitably, in carrying out the condensation, the reactants are used in the following ratios: 1 mole of high molecular weight substituted phenol, 1.5–3.0 moles of aldehyde, 0.5–1.5 moles of alkylene polyamine, and 0.5–1.5 moles of alkyl-substituted pyridine.

The high molecular weight hydrocarbon-substituted phenols suitable for use in this invention are those that have a number average molecular weight in the range from 800 to 2,500. The high molecular weight alkyl-substituted phenols are obtained by the alkylation in the presence of BF_3 or aluminum chloride or generally in the presence of a Friedel-Crafts type catalyst of phenol with C_{50} and higher carbon content polypropylenes or polybutenes. Copolymers of polypropylene with monomers copolymerizable therewith may be employed wherein the copolymer molecule contains at least 90% polypropylene units. Copolymers of butenes (butene 1, butene 2 and isobutylene) with monomers copolymerizable therewith may also be employed wherein the copolymer molecule contains at least 90% butene units.

More specifically, suitable high molecular weight alkylphenols are described in a copending application, S.N. 484,758, filed Sept. 2, 1965.

The aldehyde suitable for use in this invention is formaldehyde. Formaldehyde per se need not be used as a reactant in the process of this invention. Suitable formaldehyde yielding sources may be used such as, aqueous and alcohol solutions of formaldehyde, paraformaldehyde, and trioxymethylene. These, as well as formaldehyde itself, may be used to provide the quantities of formaldehyde required for the purposes of this invention.

Suitable alkylene polyamine reactants include ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, hexaethylene heptamine, heptaethylene octamine, octaethylene nonamine, nonaethylene decamine and decaethylene undecamine and mixtures of such amines having nitrogen contents corresponding to the alkylene polyamines according to the formula,

$$HN—(—A—NH—)_nH$$

where A is divalent ethylene and n is 1–10. Corresponding propylenepolyamines such as propylene diamine and di-, tri- tetra-, penta-propylene, tri-, tetra- and penta-amines are also suitable reactants. The alkylene polyamines are usually obtained by the reaction of ammonia and dihalo alkanes, such as dichloro alkanes.

The alkyl-substituted pyridines suitable for use in this invention are pyridines wherein the alkyl group ranges in size from C_1 to about C_8. The preferred substituted pyridines are the methylpyridines and more specifically, alpha-methylpyridine or alpha-picoline.

PREPARATION

The following procedure was used in preparing the novel additive described and claimed herein.

One mole (850 grams) of a C_{60} alkylated phenol obtained in a BF_3 catalyzed alkylation of phenol with a C_{60} polypropylene, 1 mole (93 grams) of picoline, and 1 mole (189 grams) of a tetraethylene pentamine were combined in a flask. This mixture was heated to about 35–40° C. to reduce the viscosity and to allow the components to be stirred. Two moles (162 grams) of a 37% formaldehyde solution was added slowly over a period of one hour. After stirring under a nitrogen blanket for about one additional hour the reaction products were heated. The exothermic heat generated raised the temperature to about 60° C. during the addition of the formaldehyde; however, at the end of the stirring the temperature had been reduced to about 47° C. The temperature was raised slowly over a period of about five hours to about 100° C. and the mixture was allowed to stand under a nitrogen blanket for about 12 hours. Subsequently, water was stripped from the system by heating to about 150° C. during a period of about six hours, and after nitrogen blowing at about 150° C. for about one additional hour the reaction product was cooled and removed from the flask. The product yield was about 90%.

The reaction product of the above described preparation was found to have a pH of about 10, a total base number of about 149 milligrams KOH per gram of product, a nitrogen content of about 5.84%, and an average molecular weight of about 1371. The material was dissolved in lubricating oil at concentrations shown and was then used in the following tests.

LABORATORY OXIDATION TEST

A 300 gram sample of lubricating oil containing the additives of this invention was heated to about 166° C. with stirring. A glass rod was inserted in the oil to measure the varnish formed thereon. A copper ribbon having an area of about five square inches and a ribbon of iron having an area of about ten square inches were immersed in the lubricant oil additives containing sample to function as catalysts. Intermediate inspections were made and at the end of 72 hours varnish formation on the glass rod was estimated visually and reported on a scale of 1–10, where 10 was perfectly clean. The acidity developed in the oil, the pentane insolubles, and the viscosity increase of the oil were also determined. Table I shows the results of the testing of the novel additives of this invention in accordance with the foregoing.

TABLE I.—LABORATORY OXIDATION TEST RESULTS

Additive concentration, percent	Varnish			Acidity mg. KOH per g.			Pentane insolubles (percent)		
	24	48	72	24	48	72	24	48	72
2	10	10	10	2.0	2.8	4.8	T	0.071	0.857
5	10	10	10	2.2	3.6	5.0	T	0.03	0.03

A used oil analysis was conducted to develop comparative data for various concentrations of the novel additives of this invention and the results are portrayed below in Table II.

TABLE II.—USED OIL ANALYSIS

Additive Conc.	New, 2%	Used	
		2%	5%
Vis. 100° Cs	336.9	343	401.3
Vis. 100° SSU	1516.9	1587	1860.8
Vis. 210° SSU	101.7	101.5	110.2

It is apparent from the above data that the lubricant containing the novel additive of this invention has excellent stability and provides a high degree of cleanliness.

LINCOLN ENGINE TESTS

Lubricating oils containing Mannich condensation products in accordance with this invention were tested in the Lincoln M.S.V. Test Sequence designed by Ford Motor Company. The Lincoln Sequence test procedure evaluates low temperature dispersancy characteristics of a lubrication oil. Briefly, the test consists of using the oil to be tested as a lubricating oil in a V–8 Lincoln engine under prescribed test conditions. Accordingly, five quarts of oil are placed in the crankcase and the engine is started and run in accordance with the 4-hour cycle:

	Phase 1	Phase 2	Phase 3
Duration (min.)	45	[1] 2	75
Speed, r.p.m.	500	2500	2500
Load, brake horsepower	No load	105	105
Temperature, °F.:			
Water jacket	115–120	125–130	170–175
Oil sum	120–125	175–180	205–210
Air/fuel ratio	9.5±0.5	15.5±0.5	15.5±0.5

[1] Hour.

The 4-hour cycle is repeated a total of 48 times (192 hours running time). After each 16 hours of operation the engine is shut down for eight hours. The oil level is adjusted with fresh oil to a level of five quarts. At the termination of the test, the hot oil is drained. The engine is then disassembled and examined for deposits of varnish and sludge among other observable results.

In the Lincoln M.S. Test Sequence V, after the formulated lubricant oil has been tested and the engine disassembled for inspection of the parts thereof for sludge and varnish deposits among other inspections, the total varnish and sludge ratings are made from the individual ratings of the following engine parts.

Varnish:	Sludge:
Piston	Push Rod Chamber
Rocker Arm Cover	Rocker Arm Assembly
Push Rod Cover	Rocker Arm Cover
Cylinder Walls	Oil Screen
Oil Pan	Oil Pan
	Push Rod Cover
	Timing Gear Cover
	Valve Deck

The varnish and sludge rating for each and every one of the foregoing parts is made. Then an average rating is made for each type of part, for example, the varnish ratings for each of the eight pistons are added and divided by 8 for the average piston varnish. The sum of the average ratings for each class of parts is found for both sludge and varnish. The rating of total varnish is the sum of the average ratings of the five classes of parts. A varnish rating of 7.0 or higher for each class of parts is considered to be passing.

The rating of total sludge is the sum of the average ratings for the eight classes of parts multiplied by 5/8 since the perfect total sludge rating is 50. The perfect total varnish rating is also 50.

Lincoln Engine Tests No. 1, No. 2, and No. 3

A triple Lincoln engine test was run on a lubricating oil containing 2.4% by weight of the novel additive of this invention along with 3% by weight of a high temperature detergent, 3% by weight of a high base sulfonate, and 1% by weight of a zinc dialkyl dithiophosphate oxidation inhibitor. All of the ingredients except the additive of this invention are readily available in the commercial marketplace. The results of the tests are shown below in Table III.

TABLE III.—LINCOLN ENGINE TEST RESULTS

Test No.	Sludge rating	Average rating	Oil ring plugging (percent)	Oil consumption
1	46	46	0	Low.
2	40	40	0	0.
3	43	39	5	Average.

Lincoln Engine Test No. 4

This test was conducted on a commercially available lubricating oil with 3% by weight of a high temperature detergent, 3% by weight of a sulfonate anti-rust agent, 1.1% by weight of a zinc dialkyl dithiophosphate oxidation inhibitor, and a 0.25% by weight of an anti-wear agent. The oil formulation contained at 2.4% by weight of the novel additive of this invention. The results obtained are as follows in Table IV.

TABLE IV.—Lincoln engine test results

Test No.	4
Sludge rating	43
Average rating	39
Oil ring plugging (percent)	0
Oil screen plugging	5

FORD 289 ENGINE TESTS

Two tests designated Test No. 5 and Test No. 6 were conducted on lubricating oils of different formulations in the Ford 289 cubic inch displacement engine in a manner similar to the above described Lincoln tests, each of these tests are well-known to those of ordinary skill in the art.

289 Engine Test No. 5

This test was conducted on a lubricating oil formulation containing 3% by weight of a high-temperature detergent, 3% by weight of a sulfonate anti-rust agent, 1% of a zinc dialkyl dithiophosphate oxidation inhibitor, and 0.25% of an anti-wear agent, all readily available commercially. This formulation also contained 2.4% of the novel additive of this invention. The results obtained in this test are as follows in Table V:

TABLE V.—Ford 289 engine test results

Test No.	5
Sludge rating	47
Average rating	45
Oil ring plugging, percent	0
Oil screen plugging	0

289 Engine Test No. 6

This lubricating oil formulation contained about 9.22% by weight of a polymethacrylate viscosity index improver, about 3.37% by weight of a high-temperature detergent, about 3.66% by weight of a sulfonate anti-rust agent, about 1.27% by weight of a zinc dialkyl dithiophosphate oxidation inhibitor, and about 0.315% by weight of an anti-wear agent, all readily available commercially. The formulation also included about 2.4% by weight of the novel additive of this invention. The results of the test were as follows in Table VI:

TABLE VI.—Ford 289 engine test results

Test No.	6
Sludge rating	46.8
Average rating	45.05
Oil ring sticking	None
Oil ring plugging	None
Lifter sticking	None
Oil screen plugging	None

The dispersants prepared as disclosed herein can be used as addition agents in lubricating oils and especially in lubricating oils for use in internal combustion engines. The addition agents impart excellent low-temperature dispersancy characteristics to the lubricating oil. Although amounts of the dispersancy addition agent may be varied as desired, it is believed advantageous to use at least about 1 weight percent and up to 10 weight percent of the addition agent of this invention and preferably 2–5 weight percent in a suitable lubricating oil.

Although the preferred lubricating oils are the mineral lubricating oils, the use of the additive compositions is not restricted thereto. Other lubricating oil bases can be used, such as hydrocarbon oils, both natural and synthetic, for example, those obtained by the polymerization of olefins, as well as synthetic lubricating oils of the alkylene oxide type and the mono- and polycarboxylic acid ester type, such as the esters of adipic acid, sebacic acid, azelaic acid; it is also contemplated that various other well-known additives, such as anti-oxidants, anti-foam agents, pour point depressors, extreme pressure agents, corrosion inhibitors, anti-wear agents, etc., may be incorporated in lubricating oils containing the additives of our invention.

Concentrates of a suitable oil base containing more than 10 percent, for example, up to 75 percent or more, of the additive of this invention alone or in combination with other additives may be prepared and can be used for blending with hydrocarbon oils or other oils in the proportions desired for the particular conditions of use to give a finished lubricating product containing the additives of this invention. In order to exemplify the use of the reaction products prepared in accordance herewith as low dispersancy lubricating oil addition agents, examples of formulated lubricating oils containing such reaction products were prepared.

While in the foregoing specification this invention had been described in relation to preferred embodiments thereof, and many details have been set forth for the purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to other embodiments and that many of the details set forth herein can be varied considerably without departing from the basic principles of the invention.

Having described the invention, what is claimed is:

1. The condensation product of (a) formaldehyde, (b) an alkyl substituted phenol wherein the alkyl substituent contains at least 50 carbon atoms, (c) an alkyl substituted pyridine wherein the alkyl substituent contains from 1 to 8 carbon atoms, and (d) an alkylene polyamine having the formula:

$$HN—(A—NH—)_nH$$

wherein A is a divalent ethylene or propylene group and n is 1–10, said reactants being used in the ratios of 1.5–3.0 moles of formaldehyde, 1 mole of alkyl substituted phenol, 0.5–1.5 moles of alkyl substituted pyridine, and 0.5–1.5 moles of alkylene polyamine.

2. The product defined in claim 1 wherein the alkyl substituted phenol has a number average molecular weight of from 800 to 2,500.

3. The product defined in claim 2 wherein the alkyl substituent for the phenol is derived from either polypropylene or polybutene.

4. The product defined in claim 3 wherein the alkyl substituted pyridine is either alpha picoline or alpha methyl pyridine.

5. A composition comprising a major portion of a lubricating oil and from about 1–10 weight percent of the condensation product of (a) formaldehyde, (b) an alkyl substituted phenol wherein the alkyl substituent contains at least 50 carbon atoms, (c) an alkyl substituted pyridine wherein the alkyl substituent contains from 1 to 8 carbon atoms, and (d) an alkylene polyamine having the formula:

$$HN—(A—NH—)_nH$$

wherein A is a divalent ethylene or propylene group and n is 1–10, said reactants being used in the ratios of 1.5–3.0 moles of formaldehyde, 1 mole of alkyl substituted phenol, 0.5–1.5 moles of alkyl substtiuted pyridine, and 0.5–1.5 moles of alkylene polyamine.

6. The composition defined in claim 5 wherein the alkyl substituted phenol has a number average molecular weight of from 800 to 2,500.

7. The composition defined in claim 6 wherein the alkyl substituent for the phenol is derived from either polypropylene or polybutene.

8. The composition defined in claim 7 wherein the alkyl substituted pyridine is either alpha picoline or alpha methyl pyridine.

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PATRICK P. GARVIN, *Primary Examiner.*

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