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**GASOLINE LUBRICATING OILS OR ORGANOMETALLIC ANTIKNOCK FLUIDS CONTAINING A MIXTURE OF MONO-ALKYLPHENOL CONDENSATION PRODUCTS**

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This invention relates to improved gasoline and antiknock fluid compositions. In particular, this invention relates to gasoline, antiknock fluid and engine lubricating oil containing a phenol-carbonyl compound reaction product, resulting in reduced exhaust emissions when such engine lubricating oil, gasoline, or a gasoline containing such fluid, is used in an internal combustion engine.

In recent years, extensive research has been devoted to the alleviation of air pollution in many metropolitan areas. Part of this effort has been directed to methods of reducing the unburned hydrocarbons emitted with the exhaust gas of internal combustion engines. Such unburned hydrocarbons tend to react with other atmospheric substituents to substantially contribute to air pollution and to cause smog in certain communities.

The quality and quantity of unburned and partially oxidized hydrocarbons vary widely, depending on vehicle operating conditions and upon the conditions of maintenance of the engine. For example, under idle conditions the concentration of unburned hydrocarbons in the exhaust gas stream may be as low as 300 parts per million, where as under decelerating conditions the concentration may be over 5000 parts per million. Moreover, depending on operating conditions, a variety of partial oxidation products are present in the exhaust stream. It has also been found that the amount of unburned hydrocarbons emitted by a new engine increases with engine running time until an equilibrium is reached and that this increase is due to the build-up of deposits in the combustion chamber of the engine.

An examination of the published literature reveals that up to now the only means suggested to alleviate this problem have been to (a) modify the carburetion so as to more efficiently use the fuel, thereby lowering the emission of unused or partially used hydrocarbons and (b) trap or further oxidize the exhaust emissions in the muffler or muffler area; e.g., in the use of such devices as catalytic converters, after-burners, absorbers (liquid washing devices), porous solid absorbers, condensers, etc. These proposed solutions are only partially effective and do not reduce the amount of emitted hydrocarbons to the point where pollution and smog problems are effectively eliminated.

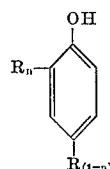
Accordingly, it is an object of this invention to provide a new approach to the problem of reducing exhaust emissions and combustion chamber deposits. More particularly, it is an object of this invention to provide engine lubricating oil, gasoline, and fluids for use in gasoline, containing an additive that has the remarkable effect of reducing exhaust emissions and combustion chamber deposits when such gasoline is used in an internal combustion engine. It is another object of this invention to provide for the operation of a spark-ignited internal combustion engine by using such engine oil as a lubricant or such gasoline as fuel for such engines. It is a further object of this invention to provide such engine lubricating oils, gasolines and fluids in which said additive is the reaction product of a phenol and a carbonyl compound. Other objects of this invention will become apparent from the ensuing description.

The above and other objects of this invention are accomplished by providing a composition comprising (a)

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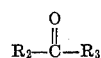
a carrier selected from the group consisting essentially of engine lubricating oil, gasoline and an organometallic antiknock fluid and (b) a phenol-carbonyl reaction product obtained by the condensation reaction of (1) a phenol having the formula

I



wherein R is a hydrocarbon radical having from 1 to about 12 carbon atoms and n is selected from 0 and 1; and (2) a carbonyl compound having the formula

II



wherein R<sub>2</sub> and R<sub>3</sub> are each independently selected from the group consisting of hydrogen, alkyl of from 1 to about 6 carbon atoms and aryl of from 6 to about 12 carbon atoms.

In Formula I, the hydrocarbon radical R is preferably selected from alkyl of from 1-12 carbon atoms, cycloalkyl of from 6-12 carbon atoms, aryl of from 6-12 carbon atoms and aralkyl of from 7-12 carbon atoms. The alkyl substituents may be unsaturated, for example, olefinic, but it is preferable that they be saturated, or paraffinic.

Examples of phenols useful in this invention include: 4-(4-methylcyclohexyl) phenol; 2-(o-methylphenyl) phenol; 2-(2-ethyl-4-n-butylcyclohexyl) phenol; 2-(2-ethyl-4-n-propylcyclohexyl) phenol; 2-methylphenol; 2-ethylphenol; 4-methylphenol; 4-ethylphenol; 2-(3'-heptylphenol); 4-(2,6-diethylphenyl) phenol; 2-(p-ethylphenyl) phenol; 4-(α,α-dimethyl-p-ethylbenzyl) phenol; 2-benzylphenol; 2-(α-methylbenzyl) phenol; 2-(α,α-dimethylbenzyl) phenol; 4-benzylphenol; 4-(α-methylbenzyl) phenol; 4-(α,α-dimethylbenzyl) phenol; 4-(2'-decyl) phenol; 4-(3'-decyl) phenol; 2-(4'-dodecyl) phenol; 4-(2'-dodecyl) phenol; 2-(α-ethyl-α-methyl-p-ethylbenzyl) phenol; 4-(3,5-di-n-propylcyclohexyl) phenol; 2-(α-n-propylbenzyl) phenol; 4-(p-n-butylphenyl) phenol; 2-n-heptylphenol; 2-(p-n-propylphenyl) phenol; 4-(p-amylphenyl) phenol; 2-(o-cyclohexylphenyl) phenol; 4-(4-phenylcyclohexyl) phenol; 2-(4-ethylcyclohexyl) phenol; 2-cyclohexylphenol; 4-phenyl; 2-phenylphenol; and 4-cyclohexylphenol.

It is preferred to use phenols in which the substituent is an alkyl group, particularly an alpha branched alkyl group of from 3 to 8 carbon atoms. Such phenols include: 2-isopropylphenol, 4-sec-butylphenol, 2-tert-butylphenol, 4-sec-amylphenol, 4-tert-amylphenyl, 2-sec-hexylphenol, 4-sec-octylphenol, 4-sec-heptylphenol, 4-tert-butylphenol and 4-tert-octylphenol. Such phenols are generally more effective and more readily obtainable. It is particularly preferred to use alkylphenols in which the substituent is in the ortho position such as 2-isopropylphenol, 2-sec-butylphenol, 2-tert-butylphenol, 2-sec-amylphenol, 2-tert-amylphenol, 2-sec-hexylphenol, 2-sec-heptylphenol, 2-tert-octylphenol and ortho-positioned isomers thereof. Such particularly preferred phenols are most effective, when reacted with a carbonyl compound, in producing a product that reduces exhaust emissions. They are readily available and easily reacted. The most particularly preferred phenol is 2-tert-butylphenol which, upon reaction with a carbonyl compound, particularly formaldehyde, produces an extremely effective exhaust emission reducing agent.

The preferred carbonyl compounds are the simple aldehydes and ketones. The preferred aldehydes are the low molecular weight aliphatic aldehydes having from 1 to about 7 carbon atoms and the low molecular weight

aromatic aldehydes containing from 7 to about 13 carbon atoms. Examples of the aliphatic aldehydes are formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, enanthaldehyde, and the like. Highly preferred aliphatic aldehydes are those containing from 1 to about 3 carbon atoms, as these aldehydes are most easily reacted and yield more effective products. Examples of preferred aromatic aldehydes are benzaldehyde, 3,5-diisopropyl benzaldehyde, p-hexyl benzaldehyde, p-phenyl benzaldehyde, and the like.

Examples of ketones that can be used include acetophenone, benzophenone, acetone, methylethyl ketone, diethyl ketone, ethylpropyl ketone, phenylhexyl ketone, p-hexylphenyl hexyl ketone, dihexyl ketone, di-p-hexylphenyl ketone, and the like. The more preferred ketones are the low molecular weight aliphatic ketones containing from 3 to about 7 carbon atoms. Examples of these more preferred ketones are acetone, methylethyl ketone, diethyl ketone, ethylpropyl ketone, and dipropyl ketone. Such ketones, and particularly acetone, are among the most preferred ketones that may be used in this invention.

Of the carbonyl compounds, formaldehyde is particularly preferred as a reactant as it is readily available, inexpensive and yields exhaust emission reducing agents on reaction with a phenol, particularly 2-tert-butylphenol, which are the most effective.

In the most preferred embodiment of this invention the exhaust emission reducing agent to be used is that prepared from the reaction of formaldehyde and 2-tert-butylphenol.

In preparing the products of this invention, the mole ratio of the carbonyl compound reactant to the phenol reactant can be from about 0.1:1 to about 20:1. It is preferred that from about 0.5 to about 10 moles of carbonyl compounds per mole of phenol be used as these ratios yield the most effective products. In general, carbonyl compound: phenol ratios of 0.5 to 1.5:1 and 7 to 9:1 are preferred as these two ranges yield the most effective products, with the lower range being particularly preferred. When the lower range, 0.5 to 1.5:1 is used, less product need be added to the gasoline to effect reductions in exhaust emissions and combustion chamber deposits.

The condensation of the carbonyl compound with the phenol can be conveniently carried out in a solvent, although a solvent is not required to produce an effective product. Preferred solvents include inert aliphatic or aromatic hydrocarbons such as isooctane, heptane, pentane, toluene, xylene, mixed aliphatic hydrocarbons boiling from about 100 to 150° C., and other such solvents that can be evaporated or distilled from the product after the reaction. Aliphatic alcohols having from 1-4 carbon atoms can be used, such as methanol, ethanol, n-propanol, isobutanol, isopropanol, and other isomeric butanols, or mixtures thereof. Water can also be used.

When using a solvent a preferred quantity is from about one-half to about five parts of solvent per part of phenol, preferably, from one to two parts of solvent per part of phenol.

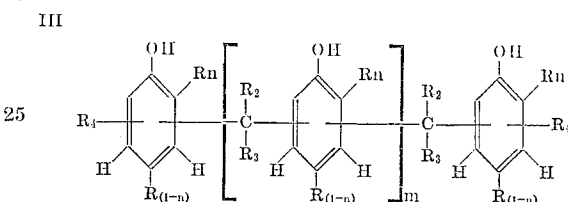
The condensation reaction is catalyzed by either an acid or base. Acid catalysts that can be employed in the condensation can be either mineral acids or organic acids, but mineral acids are preferred such as sulfuric acid, hydrochloric acid, orthophosphoric acid, meta-phosphoric acid and the like. An especially preferred mineral acid is sulfuric acid. Of the organic acids the low molecular weight mono- or dicarboxylic acids are preferred, particularly those containing from 1 to about 20 carbon atoms. Particularly preferred organic acids include such low molecular weight aliphatic acids as formic acid, acetic acid, oxalic acid, propionic acid, and the like. A most preferred organic acid is oxalic acid. Another class of acid catalysts that can be employed in preparing the products of this invention are sulfonated hydrocarbons such as benzene sulfonic acid, toluene sulfonic acid, xylene sul-

fonic acid, and the like. Mixtures of catalysts can also be used.

When using a base catalyst the inorganic metal hydroxides are preferred, particularly the water-soluble metal hydroxides. The most preferred base catalysts are sodium hydroxide and potassium hydroxide. The quantity of acid or base catalysts employed can range from a ratio of about 0.01 to about 0.5 mole of catalysts per mole of phenol. A preferred catalyst range is from about 0.05 to about 0.2 mole of catalysts per mole of phenol and particularly 0.1 mole of catalysts per mole of phenol.

The reaction can be conveniently conducted at reflux or at a temperature of about 70 to 150° C. at reaction times of from ½ hour to about 10 hours or more. At temperatures over the reflux temperature, a pressure vessel can be used. A preferred reaction temperature is at reflux at reaction times of from about 1 to about 3 hours, most preferably 2 hours.

In general, the products of this invention have the structure:



wherein  $n$ ,  $R$ ,  $R_2$  and  $R_3$  are as described following Formulas I and II above,  $m$  can range from 0-20 and  $R_4$  is selected from the group consisting of hydrogen, alkyl radicals containing from 1 to 7 carbon atoms and aryl radicals containing from 7 to 13 carbon atoms. It is preferred that  $m$  be from 1 to about 4, such products being generally more effective than the others. It is particularly preferred that  $m$  be from 0-2 and most particularly about 0, since such products are exceptionally more effective than the others.

These products are ortho- or para-substituted phenol/aldehyde or phenol/ketone condensation products wherein the substituted phenol units are connected by a substituted or unsubstituted (where formaldehyde is a reactant) methylene bridge through their ortho or para positions. Where para-substituted phenols are used as reactants, they are connected through the ortho position. Where ortho-substituted phenols are used, they are connected through positions selected, in a random manner, from the ortho and para positions. (Very little bridging occurs at the meta positions due to the relative inactivity of such positions compared to the ortho and para positions.) The random manner in which the location of the methylene bridge varies, for orthoalkylated phenols, between the ortho and para positions is shown in the above Formula III by having the bonds on the methylene bridge terminate in an indeterminate position while showing the meta positions as blocked with hydrogen substitution. Thus such indeterminate bonding location of the methylene bridge is selected from the remaining ortho and para positions.

The following examples, in which all parts are by weight, illustrate the preparation of products of this invention.

#### Example 1

A reaction vessel equipped with means for charging and discharging liquids and solids, gas inlet and outlet means, temperature measuring devices, heating and cooling means, means for agitation and means for condensing vapors, was flushed with nitrogen. To the vessel were then added 354 parts of isopropanol and 11 parts of methanol. Fourteen parts of 85 weight percent potassium hydroxide were then added with stirring and, after solution, 300 parts of 2-tert-butylphenol and 252.0 parts (4 moles per mole of phenol) of paraformaldehyde were added. The reaction mass was heated to reflux for two

hours, cooled to about 25° C., neutralized with 29 parts of glacial acetic acid (end point indicated by color change from purple to amber) and stripped of alcohol to a temperature of 100° C. Without cooling, 900 parts of toluene were added and the resulting mixture cooled to 30–35° C. and washed with 170 parts of water twelve times until neutral. The toluene was then stripped off to a temperature of about 50° C. at 65 mm. of pressure and then further stripped to 100° C. at 48 mm. pressure. The vessel was vented with nitrogen and the product was filtered while hot to yield a highly viscous liquid product of this invention. The molecular weight of the product was determined by use of a vapor phase osmometer (as discussed in a paper by R. Pasternak, P. Brady and H. Ehrmantraut, given at the 13th Chem. Eng. Congress in June 1961 at Frankfurt am Main) and was found to be 556, indicating that the product had a formula as in Formula III where  $m$  is about 1.

#### Example 2

The preparation of Example 1 was repeated and a product obtained having a molecular weight, by vapor phase osmometer, of 564.

#### Example 3

The preparation of Example 1 was repeated except that twice as much paraformaldehyde (8 moles per mole of phenol) was used per part of phenol. A product was obtained having a molecular weight, by vapor phase osmometer, of 423.

#### Example 4

The preparation of Example 1 was repeated except that one-fourth as much paraformaldehyde (1 mole per mole of phenol) was used per part of phenol. A product was obtained having a molecular weight, by vapor phase osmometer of 318, indicating that the product had a formula as in Formula III where  $m$  is 0.

Tests were run to illustrate the unusual and beneficial effects of the products of this invention on reducing engine combustion chamber deposits and exhaust emissions. In such tests, an Oldsmobile type single cylinder engine with a 10.0:1 compression ratio is used, using Super Shell, 10W-30 ashless oil and a 26% aromatic Indolene fuel containing 3.0 ml. commercial TEL per gallon (containing 0.5 theory bromine as ethylene dibromide and 1.0 theory chlorine as ethylene dichloride).

**Engine preparation.**—Before each test, the combustion chamber, valves and valve parts are cleaned of deposits and the valves are reseated. The old oil is drained, the oil pan is flushed with new oil and then filled with new oil. A new AC-45 spark plug is installed and the fuel lines are flushed with new test fuel.

**Start of test procedure.**—The engine is started on iso-octane, from a fuel burette, at 50 percent wide open throttle, at a speed of 1370 r.p.m., an air/fuel ratio of about 13.3 (about 88 percent stoichiometric) and with an ignition timing of 15° BTC. These conditions are maintained until the water and oil sump are at 165±5° F. and the carburetor air is at 110±5° F. At this condition exhaust measurements are made for hydrocarbon and carbon monoxide so as to detect any engine changes compared to other tests in the same engine. Hydrocarbon measurements are made with a Beckmann 109 Flame Ionization Hydrocarbon Detector. Carbon monoxide is measured with a Beckmann 15A Non-Dispersive Infrared Analyzer.

The engine is then switched to the test fuel and the air/fuel ratio is adjusted to 88 percent of the stoichiometric air/fuel ratio required by the test fuel. Fuel flow time is measured from a fuel burette and must be equal to a precalculated value. At this time exhaust hydrocarbon emission measurements are made, giving a start-of-test result, whereupon the engine is shut down and the oil level zeroed.

**Time accumulation schedule.**—The engine is restarted

with test fuel on a cycling schedule alternating between the following conditions:

Time, seconds.....	45	135
Speed, r.p.m.....	750-850	1,370
Load.....	None	1/50%
Air/fuel ratio.....	11, 3±0.2	<sup>2</sup> A/F±0.2
Ignition timing.....		15° BTC
Oil sump, ° F.....		165±5
Water, ° F.....		165±5
Carburetor air, ° F.....		110±5

<sup>1</sup> W.O.T. Air Flow.

<sup>2</sup> 88 percent of stoichiometric air/fuel ratio required by test fuel.

The test is run for 145 hours with emission measurements made every 24 hours.

**Periodic emission ratings.**—After about each 24 hours of test time, the engine is shut down and a new spark plug is installed. The engine is restarted with test fuel at the steady state conditions described above for "Start of test procedure." The air/fuel ratio is adjusted by measuring fuel flow time from a burette. Hydrocarbon emission measurements are taken and the engine is again shut down to zero oil level, after which it is returned to the cycling schedule.

**End of test procedure.**—At the end of 140–145 hours of test, hydrocarbon emission measurements are taken, the engine is returned to a cycling schedule for a 1–2 hour period and then shut down. The engine head is removed and deposits are scraped, removed and weighed from the intake valve stem, the exhaust valve top, the combustion chamber-valve area and the piston area.

The following results were obtained in the above tests when a 26 percent aromatic Indolene fuel, containing 3.0 ml. of commercial TEL, with and without the indicated amount of the products of Examples 1, 3 and 4 were used as the test fuel.

TABLE I

Additive	Concentration, wt. %	Hydrocarbon, p.p.m. <sup>1</sup>	Total Deposit, wt. gm.
None.....		396	16.3
Product of Ex. 1.....	0.25	301	7.8
None.....		343	16.6
Product of Ex. 3.....	0.25	269	9.4
None.....		343	16.6
Product of Ex. 4.....	0.05	173	8.6

<sup>1</sup> End of test minus Start of test results.

#### Example 5

To the reaction vessel of Example 1 were charged 315 parts of 2-tert-butylphenol and 153.6 parts of 37 percent aqueous formaldehyde. The mixture was stirred vigorously and a solution of 4.2 parts sodium hydroxide in 6.0 parts of water was added. The vessel contents were heated slowly during a one-hour period following which the reaction temperature had reached 74° C. During the following 30 minute period the temperature was raised to reflux (about 95° C.) and the mixture was allowed to reflux for about 10 minutes. The pH of the reaction mass at this point was 11.2 and an analysis for free formaldehyde indicated the presence of less than 0.1 part. Following this, the reaction mass was acidified to a pH of 3.8 using 22 parts of oxalic acid. Heating was then discontinued, the stirrer was stopped and the reaction mass was allowed to form two layers. The lower layer, containing water, salt and excess oxalic acid, was removed from the reaction vessel. The reaction mass was then vacuum distilled at 16 mm. Hg to a liquid temperature of 155° C. to remove excess water and unreacted 2-tert-butylphenol, yielding a resinous product with a softening point of 36–40° C.

#### Example 6

To the reaction vessel described in Example 1 are charged 210 parts of 2-isopropylphenol and 0.5 mole of acetaldehyde per mole of 2-isopropylphenol. The mixture is stirred vigorously and 0.01 mole of hydrochloric acid per mole of 2-isopropylphenol are added. The mix-

ture is then heated to 70° C. for 1 hour. Following this, stirring is stopped and the lower aqueous layer drained off. The remaining resin is vacuum distilled at 30 mm. Hg to a liquid temperature of 100° C., yielding a resin having a molecular weight indicative of a polymer of Formula III where  $m$  is 2.

Following the same procedure 4-(*p*-methylcyclohexyl)phenol can be reacted with caproaldehyde to yield a product which effectively reduces exhaust emissions and engine deposits. Likewise, an effective resinous product is obtained from the reaction of 4-phenylphenol with dipropyl ketone. Similarly, 2-*tert*-octylphenol can be reacted with acetophenone to yield an effective resinous product.

#### Example 7

To the reaction vessel as described in Example 1 are charged 400 parts of 4-*sec*-butylphenol, 2 moles of acetaldehyde per mole of 4-*sec*-butylphenol, 100 parts of isooctane and 0.05 mole of a 3:1 mixture of oxalic acid and toluene sulfonic acid per mole of 4-*sec*-butylphenol. While stirring, the reaction mass is heated to 150° C., under pressure, and maintained at that temperature for one-half hour. The pH of the reaction mass is then adjusted to about 3.4 by the addition of a normal sodium hydroxide solution. The aqueous layer is then removed and the reaction mixture is stripped of volatiles under reduced pressure and at a temperature of 80° C. to yield a resinous product having a molecular weight indicative of a polymer of Formula III where  $m$  is about 1.

Following the same procedure, 4-(*p*-phenylcyclohexyl)phenol can be reacted with di-*p*-hexylphenyl ketone to yield a product which reduces exhaust emissions and engine deposits. Likewise, an effective resinous product is obtained from the reaction of 2-(*o*-ethyl-*p*-*n*-butylcyclohexyl)phenol with enanthaldehyde. Similarly, 4-*sec*-amylphenol can be reacted with ethylpropyl ketone to yield an effective product.

#### Example 8

To the reaction vessel described in Example 1 are added 225 parts of 4-*tert*-amylphenol, 200 parts of ethanol, 10 moles of propionaldehyde per mole of 4-*tert*-amylphenol and 0.2 mole of acetic acid per mole of 4-*tert*-amylphenol. After stirring, the reactants are heated, under pressure, to 90° C. for one hour, followed by reflux for six more hours. The reaction mixture is then neutralized with ethanolic sodium hydroxide and the alcohol distilled off to yield a resinous product having a molecular weight indicative of a polymer of Formula III where  $m$  is about 10.

Following the same procedure, 2-(*p*-ethylphenyl)phenol can be reacted with benzophenone to yield a product which reduces exhaust emissions and engine deposits. Likewise, an effective resinous product is obtained from the reaction of 2-(4'-dodecyl)phenol with dibexyl ketone. Similarly, 2-( $\alpha$ -methylbenzyl)phenol can be reacted with 3,5-diisopropyl benzaldehyde to yield an effective product.

#### Example 9

To the reaction vessel described in Example 1 are charged 300 parts of 2-*sec*-hexylphenol, 200 parts of toluene, 3 moles of butyraldehyde per mole of 2-*sec*-hexylphenol and 0.12 mole of metaphosphoric acid per mole of 2-*sec*-hexylphenol. While stirring, the mixture is heated to about 90° C. and held at that temperature for 3 hours. The acidity is neutralized with normal aqueous sodium hydroxide and the water phase separated. The product is then washed with water and the toluene distilled off to yield a resinous product having a molecular weight indicative of a polymer of Formula III where  $m$  is about 5.

Following the same procedure, 4-methylphenol can be reacted with methylethyl ketone to yield a product which reduces exhaust emissions and engine deposits. Likewise, an effective resinous product is obtained from the reac-

tion of 2-methylphenol with phenylhexyl ketone. Similarly, 2-*sec*-heptylphenol can be reacted with acetone to yield an effective product.

#### Example 10

To the reaction vessel employed in Example 1 are charged 200 parts of 4-*sec*-octylphenol, 50 parts of *n*-propanol, 20 moles of valeraldehyde per mole of 4-*sec*-octylphenol and 0.5 mole of xylene sulfonic acid per mole of 4-*sec*-octylphenol. While stirring, the mixture is heated to reflux and maintained at reflux for 10 hours. Following this, the reaction mass is neutralized with normal aqueous sodium hydroxide and the aqueous phase removed. The resin is washed with 100 parts of water and the *n*-propanol is distilled off to yield a resinous product having a molecular weight indicative of a polymer of Formula III where  $m$  is 20.

Following the same procedure, 2-(3'-heptyl)phenol can be reacted with *p*-hexylphenyl hexyl ketone to yield a product which reduces exhaust emissions and engine deposits. Likewise, an effective resinous product is obtained from the reaction of 4-( $\alpha$ -methylbenzyl)phenol with diethyl ketone. Similarly, 2-*tert*-amylphenol can be reacted with benzaldehyde to yield an effective product.

#### Example 11

To the reaction vessel employed in Example 1 are charged 300 parts of 4-*sec*-heptylphenol, 100 parts of xylene, 5 moles of *p*-hexyl benzaldehyde per mole of 4-*sec*-heptylphenol and 0.1 mole of formic acid per mole of 4-*sec*-heptylphenol. While stirring, the reaction mixture is heated to reflux and maintained at reflux for 5 hours. The mixture is then neutralized with normal aqueous sodium hydroxide, the aqueous phase removed and the mixture washed with water. The xylene is then removed by distillation yielding a resinous product having a molecular weight indicative of a polymer of Formula III where  $m$  is 8.

Following the same procedure, 2-( $\alpha$ -*n*-propylbenzyl)phenol can be reacted with methylethyl ketone to yield a product which reduces exhaust emissions and engine deposits. Likewise, an effective resinous product is obtained from the reaction of 2-(*p*,*n*-propylphenyl)phenol with ethylpropyl ketone. Similarly, 2-*sec*-amylphenol can be reacted with methylethyl ketone to yield an effective product.

#### Example 12

To the reaction vessel described in Example 1 are charged 136 parts of 4-(*o*,*o*-diethylphenyl)phenol, 30 parts of water, 15 moles of propionaldehyde per mole of 4-(*o*,*o*-diethylphenyl)phenol and 0.3 mole of hydrochloric acid per mole of phenol. While stirring, the reaction mixture is heated to reflux and maintained at reflux for 9 hours. The reaction mass is then neutralized, the aqueous phase is removed and the resin washed with 100 parts of water yielding a resinous product having a molecular weight indicative of a polymer of Formula III where  $m$  is 15.

Following the same procedure, 4-*tert*-octylphenol can be reacted with *p*-hexyl benzaldehyde to yield a product which reduces exhaust emissions and engine deposits. Likewise, an effective resinous product is obtained from the reaction of 4-(3'-decyl)phenol with butyraldehyde. Similarly 2-*sec*-butylphenol can be reacted with formaldehyde to yield an effective product.

As demonstrated by the data in Table I, when products of the type described above are blended with gasoline, preferably in from about 0.001 to about 5 weight percent of the gasoline, spectacular results are obtained in the reduction of exhaust emissions and combustion chamber deposits. These effects are obtained both in the presence and absence of organolead antiknock agents, in the presence or absence, together with organolead antiknock agents, or alone, of a non-lead organometallic antiknock compound and in the presence or absence of a

halohydrocarbon scavenger for the antiknock compound.

Generally, those products where the carbonyl compound: phenol reactant ratios are low (e.g. about 0.5 to 1.5:1) can be added in lesser amount (preferably about 0.01-0.1, most preferably about 0.05, weight percent) than products where such ratio is high (e.g., about 7 to 9:1). These latter products are most preferably added to yield a concentration of about 0.15-0.35, most preferably about 0.25, weight percent.

Among the organolead antiknock agents which can be present in the gasoline are lead alkyls wherein each alkyl group contains up to about 6 carbon atoms and includes compounds such as tetramethyllead, tetraethyllead, tetraisopropyllead, tetrapropyllead, tetrabutyllead, tetraamyllead, tetraoctyllead, dimethyldiethyllead, hexyltriethyllead, methyltriethyllead and the like. The phenyl and mixed phenyl-alkyl compounds such as tetraphenyl,

butane, 1,4-dichloropentane,  $\beta,\beta'$ -dibromodiisopropyl ether,  $\beta,\beta'$ -dichlorodiethyl ether, trichlorobenzene, dibromotoluenes, and in general those disclosed in U.S. Patents 1,592,954; 1,668,022; 2,365,921; 2,479,900; 2,479,901; 2,479,902; and 2,496,983. The amount of scavenger generally employed is from about 0.5 to about 2.5 theories. Mixtures of bromine and chlorine-containing scavengers can be used and in the proportions described in U.S. Patent 2,398,281.

Gasoline containing an organolead antiknock, particularly tetraethyl and/or tetramethyllead, and more particularly which also contain a halohydrocarbon scavenger are generally more greatly benefitted by inclusion of a product of this invention than other gasolines.

The following examples illustrate the gasoline compositions of this invention. The types of gasoline used are characterized as follows:

Gasoline	Paraffins Percent	Olefins Percent	Aromatics Percent	Nap <sup>h</sup> th <sup>e</sup> nes Percent	End Point, ° F.	Gravity °API	Vapor Pres- sure, p.s.i.
A.....	45.2	29.4	25.4	-----	390	59.0	8.9
B.....	70.1	15.6	14.3	-----	335	64.4	-----
C.....	39.1	21.1	17.1	22.8	426	61.4	11.7
D.....	64.8	15.1	20.1	-----	403	56.2	9.5
E.....	44.0	17.9	38.1	-----	366	54.6	7.8

trimethylphenyl, diphenyldiethyl, triphenylpropyl, etc. may also be present. Generally from about 0.5 to about 6.5 grams of lead are present per gallon of gasoline.

Among the non-lead organometallic antiknock compounds that may be present are organic compounds of a metal having an atomic number of from 25-28, said organic compounds generally being hydrocarbon-soluble, covalent, and possessing in addition to said metal, only elements selected from the group consisting of carbon, oxygen, hydrogen and nitrogen. Such compounds generally contain at least one group selected from the class consisting of cyclopentadienyl groups and the carbonyl group, and contain from about 5 to about 20 carbon atoms in the molecule. The metals are generally of atomic number 25-28; i.e., manganese, iron, cobalt and nickel. Generally from about 0.005 to about 6.5 grams of such organometallic compound are present per gallon of gasoline.

Among the manganese compounds are the cyclopentadienyl manganese tricarbonyls as described, for example, in U.S. Patents 2,818,416 and 2,818,417, including cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, manganese pentacarbonyl, and the like.

Among the nickel compounds are those described in U.S. Patent 2,818,416, including cyclopentadienyl nickel nitrosyl, methylcyclopentadienyl nickel nitrosyl, indenyl nickel nitrosyl, and the like.

Among the iron compounds are the dicyclopentadienyl iron compounds such as dicyclopentadienyl iron, bis(methylcyclopentadienyl)iron, bis(butylcyclopentadienyl)iron, and the like. Other iron compounds includes iron pentacarbonyl, butadiene iron tricarbonyl and the like.

Among the cobalt compounds are the cobalt carbonyls such as cobalt tetracarbonyl, cyclopentadienyl cobalt dicarbonyl, 1-pentyne-cobalt tetracarbonyl, cobalt pentacarbonyl mixed complexes, and the like.

Additionally, scavengers may be present, which scavengers are organic halide compounds which react with the lead during combustion in the engine to form volatile lead halides. The halogen of these scavengers has an atomic weight between 35 and 80; that is the active scavenging ingredient is chlorine and/or bromine. Such scavengers include ethylenedibromide, ethylene dichloride, carbon tetrachloride, propylene dibromide, 2-chloro-2,3-dibromobutane, 1,2,3-tribromopropane, hexachloropropylene, mixed bromoxylenes, 1,4-dibromo-

#### Example 13

To 1000 gallons of gasoline A containing 3.24 grams per gallon of tetraethyllead, 0.5 theory of ethylene dibromide and 1.0 theory of ethylene dichloride are added 18.6 pounds of the product of Example 1 to yield a gasoline composition causing less exhaust emissions and less combustion chamber deposit than a similar gasoline without the product of Example 1.

#### Example 14

To 1000 gallon of gasoline B containing 3.5 grams per gallon of a commercial antiknock fluid, which fluid contains 57.52 weight percent tetramethyllead, 6.97 weight percent methyl cyclopentadienyl manganese tricarbonyl, 16.71 weight percent ethylene dibromide and 17.60 weight percent ethylene dichloride, are added 9.3 pounds of the product of Example 2 to yield a gasoline composition of this invention.

#### Example 15

To 1000 gallons of gasoline C containing 2.16 grams per gallon of a commercial TEL fluid, which fluid contains 61.41 weight percent of tetraethyllead, and 35.68 weight percent of ethylene dibromide are added 12.4 pounds of the product of Example 3 to yield a gasoline composition of this invention.

#### Example 16

To 1000 gallons of gasoline D containing 0.028 weight percent sulfur, 2.69 grams per gallon of a commercial TEL antiknock fluid, which fluid contains 16.48 weight percent tetraethyllead, 17.86 weight percent ethylene dibromide and 18.81 weight percent ethylene dichloride, and which gasoline has a Research Octane Number of 99.4 and a Motor Octane Number of 91.2 are added 3.1 pounds of the product of Example 4 to yield a gasoline composition causing less exhaust emissions and less combustion chamber deposits than a similar gasoline without the product of Example 4.

#### Example 17

To 1000 gallons of gasoline E containing 0.65 weight percent sulfur and 2.0 grams per gallon of a commercial TML antiknock fluid, which fluid contains 50.82 weight percent of tetramethyllead, 17.86 weight percent of ethylene dibromide, 18.81 weight percent of ethylenedichloride and 12.51 weight percent of hydrocarbons and other inerts, are added 6.2 pounds of the product of Example 5.

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## Example 18

To 1000 gallons of gasoline A containing 0.03 weight percent sulfur and 2.24 grams per gallon of tetramethyllead, 0.2 weight percent of dicyclopentadienyliron and 1.0 theory of dibromobutane as scavenger are added 0.062 pound of the product of Example 6.

## Example 19

To 1000 gallons of gasoline B containing 0.03 weight percent of sulfur, 6 grams per gallon of lead as tetramethyllead and 1.0 theory of ethylene dibromide as scavenger are added 310 pounds of the product of Example 7.

## Example 20

To 1000 gallons of gasoline C containing 1 gram per gallon lead as tetramethyllead, 0.08 weight percent of cyclopentadienylnickel nitrosyl and 1.0 theory of ethylene dibromide as scavenger is added 0.62 pound of the product of Example 8.

## Example 21

To 1000 gallons of gasoline D containing 2.5 grams per gallon of a commercial antiknock fluid, which fluid contains 56.15 weight percent of a mixture of tetramethyllead, ethyltrimethyllead, diethyldimethyllead, triethylmethyllead and tetramethyllead, 17.86 weight percent of ethylene dibromide and 18.81 percent of ethylene dichloride, are added 49.6 pounds of the product of Example 9.

## Example 22

To 1000 gallons of gasoline E containing 5.0 grams per gallon of tetraethyllead, 0.23 weight percent of cobalt tetracarbonyl and 1.0 theory of propylene dibromide are added 186 pounds of the product of Example 10.

## Example 23

To 1000 gallons of gasoline A containing 4.2 grams per gallon of tetrapropyl lead and 2.5 theory of chlorine as carbon tetrachloride are added 124 pounds of the product of Example 11.

## Example 24

To 1000 gallons of gasoline B containing 3.1 grams per gallon of tetraphenyl lead are added 31 pounds of the product of Example 12.

The products of this invention can be conveniently added to antiknock fluids and added to gasoline during blending of the gasoline with the fluid. The product can be added to concentrations of any of the above-mentioned organolead and/or non-lead organometallic antiknock compounds which concentrations can optionally contain any of the above halohydrocarbon scavengers. Thus another embodiment of this invention is an antiknock fluid comprising an organometallic additive selected from the group consisting of organolead antiknock compounds and organic compounds of a metal having an atomic number of from 25-28 as described above, said fluid optionally containing a halohydrocarbon scavenger as described above and containing a product of Formula III.

The amount of exhaust emission reducing product of this invention present in the fluid can conveniently be from about 0.004 to about 280 parts of such product per part of metal (i.e. if organolead is used, per part of lead; if another organometallic antiknock is used, per part of the metal of such antiknock) depending on the amount of antiknock and such product desired in the final formulated gasoline. A preferred amount is from about 0.1 to about 5 parts of such product per part of metal.

Representative antiknock compositions of this invention are presented in Table II following. The parenthetic figures following the representative ingredients are parts by weight.

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TABLE II.—ANTIKNOCK FLUID COMPOSITIONS

	Antiknock Agent	Scavenger	Product of Examples
5	Tetramethyllead (2.67).....	None.....	1 (3.4)
	Do.....	Ethylene dibromide (226).....	2 (5.7)
	Do.....	Ethylene dibromide (94) and ethylene dichloride (99).....	3 (0.267)
10	Tetraethyllead (3.23).....	None.....	4 (16.15)
	Do.....	Ethylene dibromide (188).....	5 (62.4)
	Do.....	Ethylene dibromide (94) and ethylene dichloride (99).....	6 (0.013)
15	Tetraphenyllead (3.00).....	Mixed dibromotoluenes (200).....	7 (0.5)
	Tetraethyllead (2.70) and methylcyclopentadienyl manganese tricarbonyl (0.16).....	Mixed dibromotoluenes (125) and ethylene dichloride (99).....	8 (25.0)
	Tetramethyllead (1.99) and iron pentacarbonyl (0.01).....	Mixed dibromotoluene (150) and 1,2,4-trichlorobenzene (175).....	9 (28.0)
20	Tetraethyllead (320) and cobalt tetracarbonyl dimer (2).....	Ethylene dibromide (94) and mixed trichlorobenzene (146).....	10 (10.8)
	Tetrapropyllead (379) and dicyclopentadienylnickel (5).....	Acetylene tetrabromide (346).....	11 (30.6)
20	Methyltriethyllead (309).....	1,4-dibromobutane (216).....	12 (40.1)

The antiknock fluid compositions shown in the above table are presented for illustrative purposes only. Other such compositions will now be apparent to one skilled in the art. In all instances, the presence of the product of this invention enables the fluid to be used in gasoline with a resultant decrease in exhaust emissions.

The products of this invention can also be effectively added to the engine lubricating oil. Thus another embodiment of this invention comprises engine lubricating oil containing an exhaust emission reducing amount of a product of this invention as defined above.

To prepare lubricating oils of this invention, an appropriate quantity, from about 0.01 to about 10 weight percent, and preferably from about 0.1 to about 5 weight percent, of a product of this invention is blended with a lubricant base oil. Suitable base oils include mineral oils and synthetic diester oils such as sebacates, adipates, etc. The finished lubricants may also contain other additives such as antioxidants, viscosity index improvers, detergent-dispersants, corrosion inhibitors, antiwear agents, etc. The lubricants of this invention aid in the reduction of exhaust emissions and deposit weight by its consumption in the engine during operation.

The following examples illustrates lubricating oil compositions of this invention.

## Example 25

To 1,000 parts of a solvent refined neutral oil 95 V.I. and 200 SUS at 100° F. containing 6 percent of a commercial methacrylate Type VI approver which gives the finished formulation of a V.I. of 140 and a viscosity of 300 SUS at 100° F. is added 10 weight percent of the product of Example 1.

## Example 26

To an additive-free solvent refined crankcase lubricating oil having a viscosity index of 95 and an SAE viscosity of 10 is added 0.01 weight percent of the product of Example 2.

## Example 27

To 100,000 parts of a petroleum hydrocarbon oil having a gravity of 30.3° API at 60° F., a viscosity of 178.8 SUS at 100° F. a viscosity index of 154.2 and which contains 0.2 percent sulfur, is added 0.1 weight percent of the product of Example 3. The resulting oil allows the reduction of exhaust emissions and combustion chamber deposits.

## Example 28

To 100,000 parts of a commercially available pentaerythritol ester having a viscosity at 100° F. of 22.4 centistokes, and known in the trade as "Thermoflex 600" is added 5.0 weight percent of the product of Example 4.

## Example 29

To 100,000 parts of dioctyl sebacate having a viscosity of 210° F. of 36.7 SUS, a viscosity index of 159 and a molecular weight of 426.7 is added 0.25 weight percent of the product of Example 5.

I claim:

1. A composition selected from the group consisting of engine lubricating oil, gasoline and organometallic antiknock fluid, said composition containing an exhaust emission reducing amount of a resinous product obtained by reacting 2-tert-butylphenol with formaldehyde wherein the mole ratio of formaldehyde to 2-tert-butylphenol is from about 7:1 to about 9:1.

2. Gasoline containing a tetraalkyllead antiknock agent a halohydrocarbon scavenger therefor and from about 0.15 to about 0.35 weight percent of a resinous product obtained from the reaction of 2-tert-butylphenol and formaldehyde, with a formaldehyde: phenol mole ratio of from about 7:1 to about 9:1.

3. An antiknock fluid composition, for addition to gasoline, comprising a tetraalkyllead compound and a halohydrocarbon scavenger therefor, containing from 0.004 to about 280 parts, per part of lead, of a resinous product obtained from the reaction of 2-tert-butyl phenol and formaldehyde, with a formaldehyde: phenol ratio of from about 7:1 to about 9:1.

4. Engine lubricating oil containing from about 0.01 to about 10 weight percent of a resinous product obtained from the reaction of 2-tert-butylphenol and formaldehyde, with a formaldehyde: phenol ratio of from about 7:1 to about 9:1.

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