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GASOLINES AND PHOSPHORUS-CONTAINING ADDITIVES THEREFOR

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6 Claims. (Cl. 44—69)

The present invention relates to novel lead-containing fuels for operation of internal combustion engines and to the operation of such engines with such fuels. More particularly, the present invention relates to novel lead-containing fuels that reduce the abnormal combustion phenomena known as "rumble" and minimize preignition in operation of internal combustion engines.

As is well known to those skilled in the art, the compression ratio of internal combustion engines has been steadily increased. Such compression ratio increases have led to increased incidence of a combustion phenomenon known as rumble which is more prevalent in engines having compression ratios of at least 10:1 and higher. It is postulated that rumble is caused by abnormally high rates of pressure rise resulting from too rapid burning of the fuel-air mixture whereby vibrations are produced in overstressed engine parts causing a low frequency thudding noise that is associated with rumble.

As is also well known to those skilled in the art, the addition of lead anti-knock agents, such as tetraethyl lead and tetramethyl lead or mixtures thereof, to increase octane ratings is a well-established practice. It is also well known that the use of leaded gasolines have disadvantages, notably the occurrence of preignition. As the term implies, preignition is the ignition of the air-fuel mixture in the cylinder before the regular, timed spark ignition whereby the engine will behave as if the spark has been advanced beyond its normal timing. Such a phenomenon is, of course, a barrier to further increases in compression ratios. Thus, the problem of preignition has become more acute because of the trend to engines of increased compression ratio.

As is contemplated herein, preignition is caused by incandescent particles of combustion chamber deposits. Such deposits consist of a mixture of carbonaceous material and lead salts formed by decomposition of the lead anti-knock compounds. The lead salts resulting from the combustion of a leaded motor fuel are complex in nature. It is believed that they include lead chloride or bromide, lead oxide and lead sulfate, as well as mixed salts thereof formed through solid-solid reactions. These lead compounds have a catalytic effect upon the oxidation of the carbon in the combustion chamber deposits. The rapid oxidation of the carbon particles causes them to glow and to remain aglow for considerable periods of time after the combustion cycle. Accordingly, these glowing particles are present during the subsequent combustion cycle and cause preignition. Although pure carbon must be heated to about 1400° F. to make it glow, in the presence of lead salts the carbon glow is initiated as much as about 700° F. lower. Thus, it will be appreciated that obviating or minimizing the catalytic oxidation effect of the lead salts will reduce preignition.

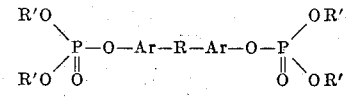
Certain phosphorus compounds are known to those skilled in the art to be effective types of compounds for rendering inert the stated catalytic effect of lead salts and, in general, it is known that a larger concentration of the phosphorus compounds is required in the fuel to minimize the rumble problem than is required to control the other forms of surface ignition. For example, in the use of a phosphorus compound such as tricresyl phosphate, 0.2 theory is normally required for the control of "wild ping" type of surface ignition whereas 0.4 to 1.0

theory is normally required to control rumble. In connection with the proportional amount of phosphorus compound to the lead compound, as used herein, "theory" is the quantity of additive required to furnish 2 atoms of phosphorus for 3 atoms of lead in the fuel to form $Pb_3(PO_4)_2$.

It has now been found that rumble and deposit-induced preignition of spark-ignition internal combustion engines can be materially reduced by addition of certain phosphorus-containing compounds and combinations thereof in leaded motor fuels and, more particularly, that, by use of the phosphorus-containing compounds embodied herein, a marked and unexpected increased activity on a phosphorus basis is obtained as compared to certain conventional phosphorus-containing additives for such purposes in leaded motor fuels.

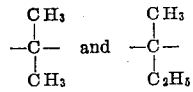
The fuels contemplated herein are mixtures of hydrocarbons suitable for use in internal combustion engines of the spark ignition type, including motor gasolines and aviation gasolines. In general, motor gasolines have an initial boiling point as low as about 80° F. and an end boiling point as high as about 440° F. and boil substantially continuously between the initial boiling point and the end boiling point. Aviation gasolines, on the other hand, are mixtures of hydrocarbons having an initial boiling point of about 80° F. and an end boiling point of about 340° F. and boiling substantially continuously between these points. Motor gasolines, at present, can, for example, contain up to about 4.0 ml. of tetraethyl lead per gallon whereas aviation gasolines can contain up to about 4.6 ml./gallon of such a material. In general, the anti-knock compound is an organic lead compound as, for example, lead tetraalkyls, such as lead tetraethyl, lead tetramethyl, and mixtures thereof, and which gasolines are commonly referred to as leaded gasolines. Furthermore, it is common practice to add to the leaded gasoline a halohydrocarbon scavenger and, typical thereof are substances such as ethylene dichloride, ethylene dibromide, acetylene tetrabromide, and mixtures thereof. It is also common practice to use a combination of ethylene dichloride and ethylene dibromide in leaded motor gasolines whereas ethylene dibromide alone is used in leaded aviation gasolines. The amounts of scavenger utilized are calculated to avoid excessive wear and corrosion of the operating parts of the engine such as exhaust valves, and achieve effective scavenging of lead deposits. Thus, in the case of leaded motor gasolines, it has been the practice to use one theory of ethylene dichloride and 0.5 theory of ethylene dibromide. On the other hand, it has been the practice to use one theory of ethylene dibromide in leaded aviation gasoline. As used herein, the term "theory," as applied to the proportional amount of scavenger to lead, is intended to mean the amount of the scavenger required to convert all the lead present into a lead salt as, for example, into a lead salt such as lead chloride or bromide.

The phosphorus-containing compounds embodied for use in practice of this invention are high molecular weight phosphates having the structural formula:

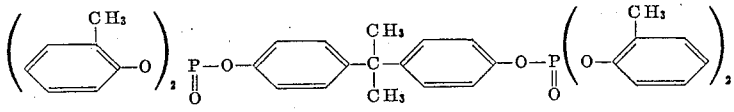


wherein R is a divalent aliphatic hydrocarbon group, straight or branch chain, Ar is a member from the group consisting of aryl and substituted-aryl in which the substituent is preferably an alkyl group or a halogen (e.g., chlorine), and R′ is the same or different members from

the group consisting of alkyl, aryl, alkaryl and halogen-substituted aryl. Preferably, in such high molecular weight phosphates, R is a lower molecular weight aliphatic hydrocarbon group containing, for example, from one to about 12 carbon atoms as in the following illustrative groups; methylene, ethylidene, propylidene, and dodecylidene, and still more preferably, divalent groups such as:

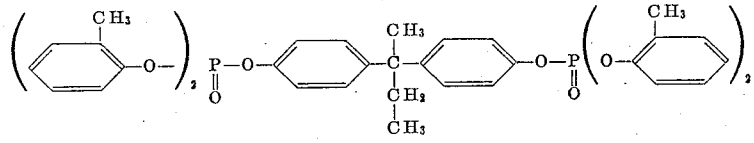


Ar is an aryl or alkaryl group such as may be derived from phenol and substituted phenols as, for example, from cresol, xylenol, isopropyl phenol, t-butyl phenol, nonyl phenol, halogen-substituted phenols such as chlorophenols, polychlorophenols, etc.; and R′ is alkyl, aryl or alkaryl, and, illustratively, methyl, isopropyl, octyl, tolyl, xylyl, t-butyl phenyl, nonyl phenyl, etc. Preferably, R′ is an aromatic group as, generally, the presence of an aromatic hydrocarbon group in the R′ positions provides compounds that are less antagonistic to the lead-containing anti-detonant additives used in gasolines. As a very specific embodiment, the present invention is carried out with a compound of the following formula:

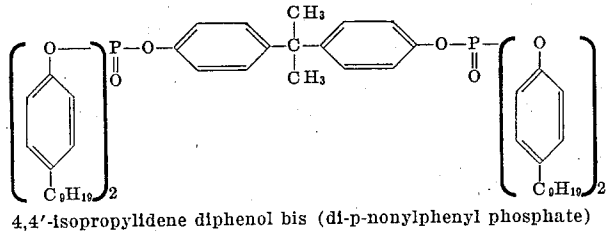


4,4′-isopropylidene diphenol bis (di-o-tolyl phosphate)

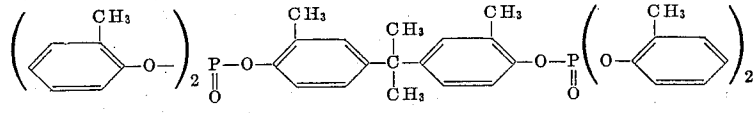
Still other compounds embodied for use in practice of this invention are the following:



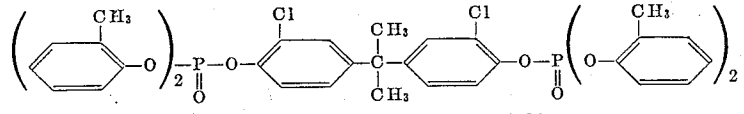
4,4′-sec-butylidene diphenol bis (di-o-tolyl phosphate)



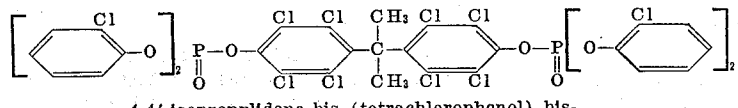
4,4′-isopropylidene diphenol bis (di-p-nonylphenyl phosphate)



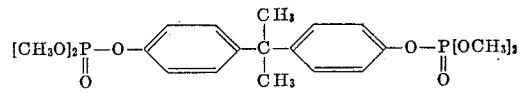
4,4′-isopropylidene bis (2-methylphenol) bis (di-o-tolyl phosphate)



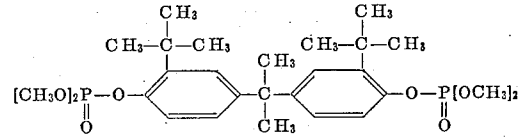
4,4-isopropylidene bis (2 chlorophenol) bis (di-o-tolyl phosphate)



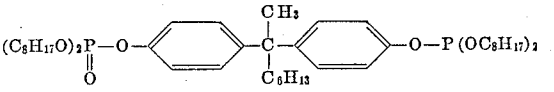
4,4′-isopropylidene bis (tetrachlorophenol) bis-(di-o-chlorophenylphosphate)



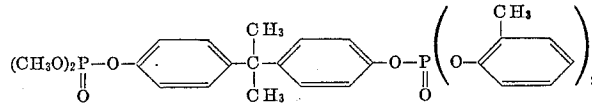
4,4′-isopropylidene diphenol bis (dimethyl phosphate)



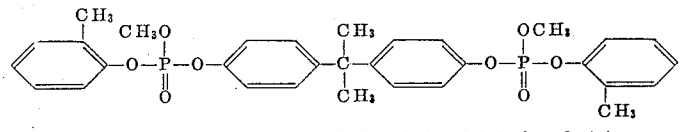
4,4′-isopropylidene bis (2-t-butylphenol) bis (dimethyl phosphate)



4,4′-(1-methylheptylidene) diphenol bis (di-octyl phosphate)



2-(dimethoxyphosphinyloxyphenyl)-2 (di (o-methylphenoxy) phosphinyloxy phenyl) propane



4,4′-isopropylidene diphenol bis (methyl, o-tolyl phosphate)

In reference to compounds of the foregoing formula wherein Ar and R′ are aryl or substituted-aryl groups, they may be synthesized by heating an appropriate phenolic compound with phosphorus oxychloride at, for exam-

ple, 80 to 300° C. depending on the particular catalyst employed. For such a process, metal halides, as $MgCl_2$ and $AlCl_3$ are particularly suitable catalysts as they permit condensation times of 6–9 hours at 200° C. Evolution of hydrogen chloride generally starts at about 100° C. and is completed at about 225° C. when anhydrous $MgCl_2$ is used as the catalyst. If desired, the reaction may be carried out in steps with isolation of the intermediates. Thus, and preferably using an excess of the phenolic reactant to drive the reaction to completion, the plural step process can be carried out as follows:

(1)

$$2R'OH + POCl_3 \xrightarrow[\Delta]{MgCl_2} (R'O)_2P(=O)Cl + 2HCl$$

(2)

$$2(R'O)_2P(=O)Cl + HO{-}Ar{-}R{-}Ar{-}OH \xrightarrow[\Delta]{MgCl_2}$$

$$(R'O)_2P(=O){-}O{-}Ar{-}R{-}Ar{-}O{-}P(=O)(OR')_2 + 2HCl$$

Purification, as desired, may include flash distillation of the crude reaction product mixture, washing with dilute caustic to neutralize any hydrogen chloride and extract partial esterification products or phenolic compounds, treatment with permanganate to improve color, and treatment with adsorbents and dehydration.

In reference to compounds of the foregoing formula wherein Ar is aryl or substituted aryl, and R' is an aliphatic group, they may be synthesized by any of several methods, one of which is as follows and involves esterification of phosphorus oxychloride with an alcohol.

(1)

$$2R'OH + POCl_3 \xrightarrow[\text{amines or vacuum}]{0-20^\circ C.} (R'O)_2P(=O)Cl + 2HCl$$

(2)

$$2(R'O)_2P(=O)Cl + NaOAr{-}R{-}ArONa \xrightarrow{10-30^\circ C.}$$

$$(R'O)_2P(=O){-}O{-}Ar{-}R{-}Ar{-}O{-}P(=O)(OR')_2 + 2NaCl$$

The alkyl phosphoryl halide may be prepared by the addition of an alcohol to phosphorus oxychloride in approximately stoichiometric amounts at 0–20° C. with removal of the evolved hydrochloric acid by application of reduced pressures or by neutralization with amines such as pyridine, ammonia, etc. Purification may be achieved by washing till neutral and fractional distillation. A second method of preparing the phosphoryl halide is by the addition of chlorine to a dialkyl hydrogen phosphite.

The alkyl phosphoryl halide may then be esterified with a phenolic compound by the Schotten-Baumann technique. The phosphoryl halide is added to a solution or suspension of the sodium arylate at 10–30° C. The ester product is separated and washed with dilute aqueous sodium hydroxide solution and water till neutral. Further purification, as desired, may be achieved by steaming to remove traces of alcohol, decolorization with permanganate solution and/or adsorbents, filtration and dehydration.

In a specific embodiment, the following procedure was used for preparation of 4,4'-isopropylidene diphenol bis (di-o-tolylphosphate).

(a) *Preparation of di-o-tolyl phosphorochloridate.*—Phosphorus oxychloride (6 m., 920 g.) plus anhydrous magnesium chloride (9 g.) were added to a 5 liter flask equipped with a thermometer, a reflux condenser, a stirrer and an addition funnel. The reflux condenser was connected to two gas wash bottles in series containing known amounts of aqueous sodium hydroxide and phenolphthalein indicator (to measure the evolved hydrogen chloride). o-Cresol (12 m., 1324 g., 98% pure) was added in portions to the flask with stirring and heating. Three hundred grams of the o-cresol were added initially; the remainder during 255 minutes as the reaction mixture was heated to 110° C. (Hydrogen chloride began to evolve at about 85° C.) Heating and stirring were continued for an additional two hours during which the temperature rose to 190° C. Nitrogen gas was passed through the reaction mixture during the last 55 minutes of this period to help expel the evolved HCl. A total of 12 moles of HCl were evolved during the reaction and were measured by absorption in the standardized aqueous sodium hydroxide solutions.

The reaction mixture was distilled under vacuum through a packed column.

Di-o-tolyl phosphorochloridate cuts distilling at 182–187° C. at 5.0 to 5.5 mm. pressure were combined. Weight of this combined material was 824 g. Analyses of this product showed 12.1% Cl and 10.5% P; theoretical analyses of di-o-tolyl phosphorochloridate are 12.0% Cl and 10.4% P.

(b) *Preparation of the 4,4'-isopropylidene diphenol bis (di-o-tolylphosphate).*—The di-o-tolyl phosphorochloridate (1 m., 296.7 g.) and bis phenol A (4,4'-isopropylidene diphenol) (0.5 m., 114.1 g.) were placed in a four-necked flask equipped with a stirrer, thermometer, reflux condenser and a dropping funnel. Anhydrous magnesium chloride (0.5 g.) was added to the mixture. All gases evolved from the reaction were passed through two wash towers containing measured amounts of aqueous sodium hydroxide solution and phenol-phthalein indicator. The mixture was heated with stirring from 25 to 215° C. during 100 minutes and then maintained at 215° C. for 25 minutes. Nitrogen was passed through the mixture at 215° C. to help expel the evolved HCl. Evolution of HCl started at about 85° C. A total of about 0.9 m. of HCl was evolved.

Four hundred cc. of benzene was added to the reaction product. It was then washed with 50 cc. of 5% aqueous hydrochloric acid; 100 cc. of 5% aqueous sodium hydroxide; 50 cc. of 0.25% aq. HCl; and finally with water until neutral. Centrifuging or adding minor amounts of petroleum ether (less than 50 cc.) were used to break the emulsions which tended to form during the washings. The solvents were then stripped from the reaction product under vacuum until a pot temperature of 210° C. at a pressure of 19 mm. Hg was attained. Weight of product was 367 g.

To further purify this material, 355 g. of the above product was dissolved in 500 cc. benzene and passed through 500 g. of Alcoa activated alumina F–20 packed in a 25" x 1⅝" column. The benzene solvent was stripped from the eluate until a pot temperature of 205° C. at 10 mm. Hg was reached. The following analyses were obtained for the purified ester.

	Found	Theoretical
Percent P	7.88	8.27
Percent C	68.83	68.98
Percent H	5.60	5.65
Mol. Wt.	765 cryoscopic; 730 vapor press.	749
Percent Cl	<.01	0

The amount of phosphorus-containing compounds used in the present invention is dependent on the lead content. Accordingly, instead of defining the amount in terms of weight or volume concentrations, it is more accurate to express the amount of phosphorus-containing compound in terms of a "theory." Such a theory is, as aforesaid, the amount of phosphorus-containing compound stoichiometrically required to react with all the lead present in the gasoline formulation to form lead orthophosphate. Thus, "0.5 theory" would indicate one-half the amount of phosphorus-containing compound stoichiometrically required to react with all the lead present. Generally, in practice of this invention, the

amount of the phosphorus-containing compound will be between about 0.02 theory and about 2.0 theory, and preferably, between about 0.1 theory and about 0.5 theory.

In addition to additives such as lead anti-knock compounds and scavengers such as halohydrocarbons, and the phosphorus compounds embodied herein, the gasoline composition can contain other additives. Thus, for example, the gasolines can include dyes, carburetor de-icing agents such as isopropyl alcohol and lauryl mercaptoacetic acid, corrosion inhibitors such as polymerized fatty acids and salts of petroleum sulfonic acids, metal deactivators such as N,N'disalicylidene-1,2-diaminopropane, anti-gum formation additives such as 2,6-ditertiarybutyl paracresol, etc.

The following examples are for the purpose of illustrating the preparation and the effectiveness, in the defined rumble and preignition tests, of the compositions of this invention. It is to be understood that this invention is not to be limited by the specific compositions of the examples or to the operations and manipulations involved. Other additives as described hereinbefore can be used as those skilled in the art will readily appreciate.

THE RUMBLE TEST

The engine used for this test is a 1956 Buick V–8 engine with a 322 cu. in. displacement. The piston crowns are modified to give a compression ratio of 11:1. Standard carburetion and ignition systems are employed. The engine is equipped with a conventional Dynaflow transmission connected to a TLC–74 D.C. dynamometer (200 H.P.). The dynamometer contains a flywheel which produces inertia characteristics like those imposed by the weight of a typical passenger car. In order to eliminate effects attributable to fluctuating conditions of intake air, it is supplied from an air conditioning system at constant temperature and humidity.

The engine is operated for 240 hours on an alternating operation schedule consisting of one hour at constant speed running at 1700 r.p.m. followed by one hour of cyclic operation between 500 and 1700 r.p.m. The engine operating conditions are set forth in Table I.

Rumble severity is determined every 24 hours during the test run by making 15 wide open throttle accelerations on isooctane +3 ml. TEL/gal. Audible ratings of rumble severity are assigned to each acceleration from the following scale:

Intensity:	Rumble value
Heavy rumble	10
Medium rumble	7.5
Light rumble	5
Trace rumble	2.5
No rumble	0

The average of the 15 ratings constitutes the daily rumble rate. An average of these daily rates (commencing with the 72 hour rating) is the over-all rumble rating, which is the reported value.

TABLE I

Operating Conditions:
Test Duration—Approx. 240 hours
Type of Operation—Alternating fixed and cyclic

Type	Fixed	Cyclic			
Duration (hrs.)	1	1	1	1	1.
Action	Run	Idle	Accel	Run	Decel.
Duration (secs.)		30	14	120	16.
Engine Speed (r.p.m.)	1,700	500		1,700	
Dynamometer Speed (r.p.m.)	1,640	400	To 1,650	1,640	To 400.
BHP-Dynamometer	15	0.6		15	
Manifold vacuum (Hg)			8 min		
Jacket coolant temp., ° F	180	180	180	180	180.
Inlet air:					
Dry bulb, ° F	105	105	105	105	105.
Wet bulb, ° F	69	69	69	69	69.
Basic ignition timing	5° BTC.	5° BTC.	5° BTC.	5° BTC.	5° BTC.

PREIGNITION TEST

This test is conducted with a Labeco 17.6 crankcase equipped with a single cylinder Olds' modified conversion assembly which includes a 1953 Oldsmobile combustion chamber mounted on a wet sleeve cylinder. The engine, in good mechanical condition, is prepared for test with clean valves, combustion chamber, and new spark plug. Following an initial one-hour warm-up, the engine is run under preset cyclic conditions continuously for a total test time of 80 hours. Performance of the test gasoline is judged by the rate of preignition counts per hour.

For the preignition test, the engine is considered ready for test if a minimum of 5.13 H.P. output (22 lbs.-Toledo scale) can be obtained on clear isooctane at the following conditions:

MAP (manifold air pressure), Hg. abs.	30"
Air:fuel ratio	13.0/1
Speed, r.p.m.	1400
Spark advance	TDC
Temperature, ° F.:	
Jacket	212
Oil	170
Air	100

Example 1

The fuel used for this example was a platinum reformate of the following properties and which contained an anti-oxidant (2,6-ditertiarybutyl paracresol), a metal deactivator (N,N'-disalicylidene 1,2-diaminopropane) and a scavenger of ethylene dichloride and ethylene dibromide.

Gravity, ° API	42.4
RVP, lbs.	4.5
Distillation, ° F.:	
Initial	92
5%	143
50%	256
90%	328
End point	410
Mercaptan sulfur, p.p.m.	3.0
Lamp sulfur, wt. percent	0.0004
Aromatics, vol. percent	69.2
Olefin, vol. percent	0.7
Saturates, vol. percent	30.1
Research octane No. (3 ml. TEL/gal.)	105.8

RUMBLE ENGINE TEST RESULTS

Run No.	Additive	Rumble Rating
1 Base Fuel	None	8.1
2 Base Fuel	0.4 theory diphenyl tolyl phosphate	6.3
3 Base Fuel	0.4 theory 4,4'-isopropylidene diphenol bis (di-o-tolyl phosphate).	1.2

As is apparent from the foregoing, the base fuel was markedly suppressed against rumble by use of an addi-

tive embodied for use herein (Run 3) as compared to the relatively small extent of suppression resulting from use of a conventional phosphorus-containing additive (Run 2) at the same 0.4 theory.

Example 2

Base gasoline composition same as in Example 1.

PREIGNITION ENGINE TESTS

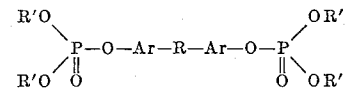
Run No.	Additive in Fuel	Preignition Rate, counts/hour
1 Base Fuel	None	83
2 Base Fuel	0.2 theory diphenyl tolyl phosphate	63
3 Base Fuel	0.2 theory 4,4'-isopropylidene diphenol bis (di-o-tolyl phosphate).	24

As is apparent from the foregoing, use of the additive embodied herein (Run 3) resulted in markedly improved performance in the preignition test as compared to the conventional additive (Run 2) at the same theory concentration.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. Gasoline containing a lead-containing anti-knock agent in an amount of up to about 4.6 ml., calculated as tetraethyl lead, per gallon of gasoline and between about 0.02 to about 2.0 theory of a phosphorus-containing compound of the following formula:



wherein R is a divalent aliphatic hydrocarbon group, Ar is alkyl-substituted aryl, and R' is a member from the group consisting of aryl, alkyl-substituted aryl and halogen-substituted aryl.

2. A composition, as defined in claim **1**, wherein R is an aliphatic hydrocarbon group of one to twelve carbon atoms.

3. A composition, as defined in claim **2**, wherein R is



4. A composition, as defined in claim **1**, wherein R' is alkyl-substituted aryl.

5. A composition, as defined in claim **1**, wherein R' is tolyl.

6. A composition, as defined in claim **1**, wherein the phosphorus-containing compound is 4,4'-isopropylidene diphenol bis (di-o-tolylphosphate).

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